# Bioaccumulation Model Introduction

LPRSA RI/FS Modeling Meeting

February 13, 2014

9:30-2:00

# Agenda

- Bioaccumulation model
  - Background information
  - Model structure
- Benthic community analysis/biologically active zone
- Calibration
  - Data
  - Approach
  - Preliminary results
- Using the model to make projections for remedial alternatives analysis
  - Dynamic model
  - Preliminary projections
- Open discussion
- Wrap up/next steps
  - Additional oversight

# BIOACCUMULATION MODEL

# Background

- The model that we'll be talking about today was developed for hydrophobic organic chemicals (HOCs) and appropriate for modeling PCBs, dioxin/furans, pesticides, etc.
  - Initially focusing on 2,3,7,8-TCDD and tetra-CBs
- The bioaccumulation model is a work in progress. The information that we are presenting today is for discussion purposes only and subject to change.
- Chemicals to be considered in bioaccumulation modeling calculations are to be selected after consultation with EPA based on three criteria*
  - elevated concentrations in LPRSA
  - shown to accumulate in organisms
  - presenting a specific ecological or human health risk
- It's possible that different models could be needed for chemicals other than HOCs

* LPR/NB Modeling Work Plan, Section 6.5.3

# A Simpler Approach for Non-Driver Chemicals

- Focus on "driver chemicals" (chemicals expected to define footprints of remedial alternatives)
- For non-driver chemicals
  - Use concentration maps to calculate SWACs
  - Superimpose remedial alternative footprints, assign replacement values within footprints, recalculate SWACs
- Estimate TC reductions, compare to risk-based thresholds
  - Rougher estimates made with simple models might be good enough for non-driver chemicals

# Background

- LPRSA model based on Arnot & Gobas (2004) model
  - Refinement of the Gobas (1993) steady state mass-balance model originally developed to describe PCB bioaccumulation in the Great Lakes food web
  - Reflects better understanding of bioaccumulation processes based on subsequent field and laboratory studies
  - Models dietary and respiratory bioaccumulation and loss processes
  - Also models metabolic loss and growth dilution

Arnot JA, Gobas FAPC. 2004. A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ Toxicol Chem* **23**:2343-2355.

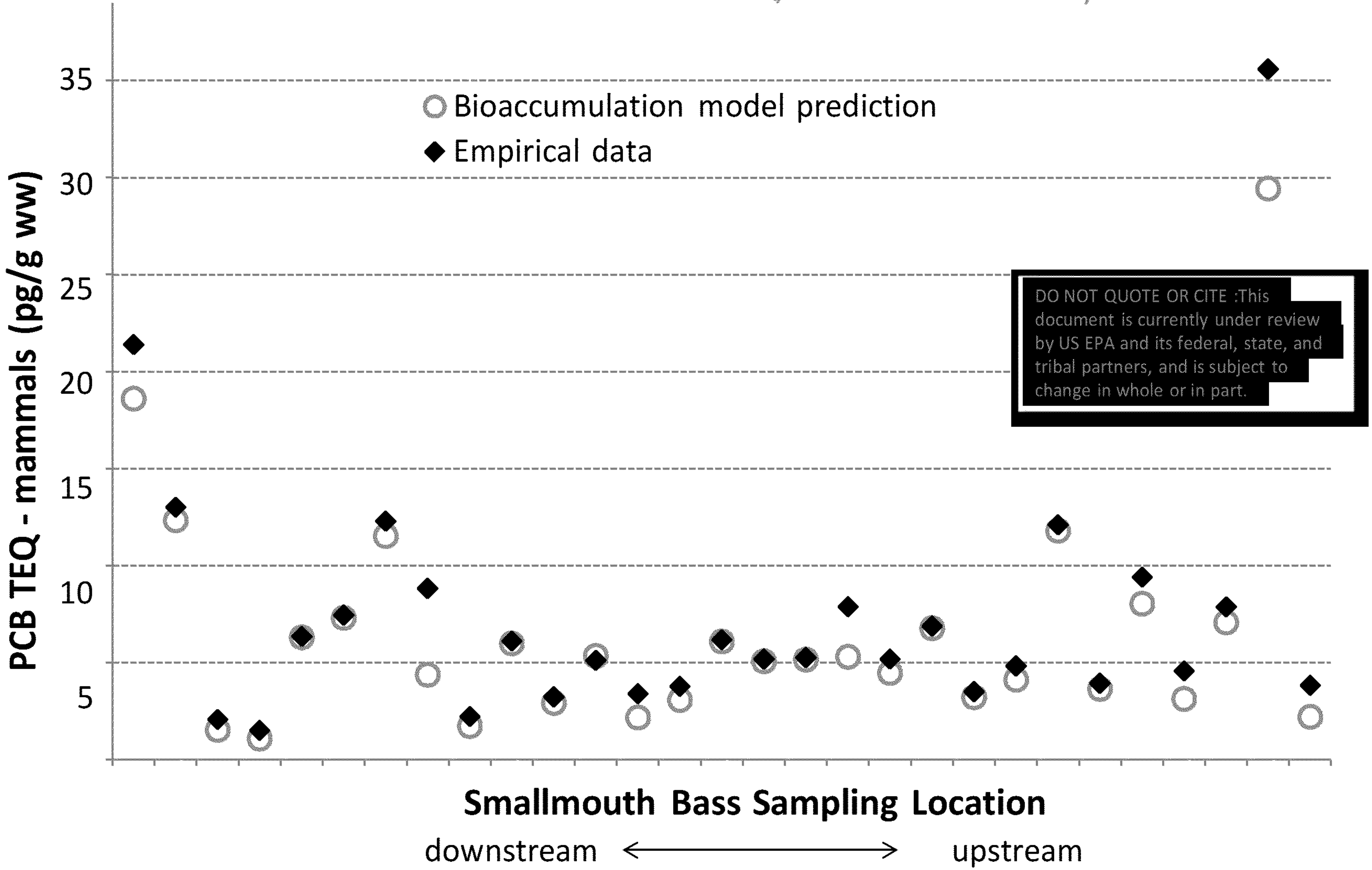
Gobas FAPC. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: Application to Lake Ontario. *Ecol Model* **69**:1-17.

# Background

- Same model & approach used by the same modeling team under EPA oversight for Lower Duwamish and Portland Harbor
  - http://www.epa.gov/region10/pdf/sites/ldw/remedial_investigation_7-9-2010.pdf
  - http://lwgportlandharbor.org/library/documents/2012-03/Draft%20Feasibility%20Study%20Appendices/Appendix%20Hb/2012-03-30_Draft%20FS_Appendix%20Hb.pdf
  - https://portal.webpe.com/portal/page/portal/LWG/CONTENT/PHCP_FILES/Documents_Under_Review/2009/2009-07-21_Draft%20Bioaccumulation%20Modeling%20Report

# PCB TEQ Measurements and Projections

## (Based on PCB 126 bioaccumulation modeling + statistical relationship between PCB 126 and PCB TEQ, Portland Harbor)



# LPRSA Model Attributes

- Static and dynamic formulations
- Flexible food web structure
- Spatially discretized
- Easily coupled with chemical fate & transport and risk models
- User-friendly interfaces (input and output)
- Excel platform facilitates sensitivity and uncertainty analyses (deterministic and probabilistic)

# Model Status

- Working draft
  - Developed CFT interface to generate bioaccumulation model inputs
  - Generated initial range estimates for model coefficients
  - Tested calibration approach
  - Calibrated the model to LPRSA tissue concentration datasets with inputs generated from preliminary CFT output
  - Developed and tested human health risk calculation interface
- Will be finalized when HST and CFT are ready
  - A lot of moving parts

# CFT Interface

[redacted]

Post-Processing

[redacted]

Pre-Processing
- Spin-up
- Sensitivity analysis tools

[redacted]

# Generating Bioaccumulation Model Inputs

## Overview of Processors

**CFT Model (RCATOX) outputs binary files**

- Water column: REAF10 & REAF11, hydrocoupling files
- Active bed: REAF44 & REAF45
- Archive bed: REAF64 & REAF65

→

**FORTRAN processors extract model output to text files**

- Water column: Read_rcaf1011_140123.f Read_gcmtran.f
- Active bed: Read_rcaf4445_130409.f
- Archive bed: Read_rcaf6465_140109.f

→

**IDL program reads extracted text files, calculates foodchain model input variables, and writes values to text file**

- Compile_foodchain_inputs.pro

# Extracting CFT Model Output
## FORTRAN Processors

- FORTRAN processors read RCATOX model output binary files and extract values to text files

| Water Column | RCATOX "Active Bed" (top 10 layers) | RCATOX "Archive Bed" (> 10 layers) |
|---|---|---|
| • Temperature<br>• Dissolved chemical concentration<br>• Dissolved organic carbon concentration<br>• Particulate chemical concentration<br>• Particulate organic carbon concentration including phytoplankton<br>• Total chemical concentration<br>• Total suspended solids concentration | • Dissolved chemical concentration in porewater<br>• Dissolved organic carbon concentration in porewater<br>• Particulate chemical concentration<br>• Particulate organic carbon concentration<br>• Total chemical concentration<br>• Sediment concentration<br>• Individual layer thickness | • Particulate organic carbon concentration<br>• Total chemical concentration<br>• Sediment concentration<br>• Individual layer thickness |

# Calculating Foodchain Model Inputs
## IDL Processor

- Reads in model output and exposure zone definitions
- Calculates depth-averages CFT variables in water column and bed
  - Depth averages are weighted by layer thickness in both the water column and sediment bed
  - If using more than 10-layers in the bed, assumes the fraction dissolved and particulate below layer 10 is the same as in layer 10
- Calculates foodchain model input variables
  - Averages in space for defined exposure areas (22 “segments”)
  - Averages in time (monthly)
- Writes foodchain inputs to a text file, which is used to populate spreadsheets

# IDL Program

## Calculating Water Column Variables

- **TW**: Water temperature
- **CWB**: Depth-average bioavailable concentration in water column
    - $CWB = C_{wc,diss,1\text{-}10}/(1 + (K_{ow} \times 0.08 \times DOC_{wc}))$
- **CPART**: Depth-average concentration in water column particulates
    - $CPART = C_{wc,part,1\text{-}10}/TSS_{wc,1\text{-}10}$
- **CPW**: Depth-average concentration of suspended solids
    - $CPW = TSS_{wc,1\text{-}10}$
- **OCPART**: Depth-average organic carbon content of water column particulates (fraction of total)
    - $OCPART = POC_{wc,1\text{-}10}/TSS_{wc,1\text{-}10}$
- **CPART_DET**: Concentration in particulates in the bottom layer of the water column for detritivores
    - $CPART\_DET = C_{wc,part,10}/TSS_{wc,10}$

***Note: Unit co[redacted]ersion factors omitted for clarity***

# IDL Program

## Calculating Sediment Bed Variables

- **CSD**: Depth-average concentration (between layers 1 and X) in sediment porewater
  - $CSD = (C_{bed,diss,1\text{-}X}/\Phi)/\rho_{water}$
    - $\Phi = TSS_{bed,1\text{-}X}/\rho_{sed}$ (porosity)
      - » $\rho_{sed} = 2.65$ kg/L (sediment specific gravity)
- **CST**: Depth-average concentration in sediment solids
  - $CST = (C_{bed,part,1\text{-}X}/TSS_{bed,1\text{-}X})$
- **OCSS**: Depth-average organic carbon content of sediment (fraction of total)
  - $OCSS = POC_{bed,1\text{-}X}/TSS_{bed,1\text{-}X}$

***Note: Unit conversion factors omitted for clarity***

# IDL Program

## Depth Averaging

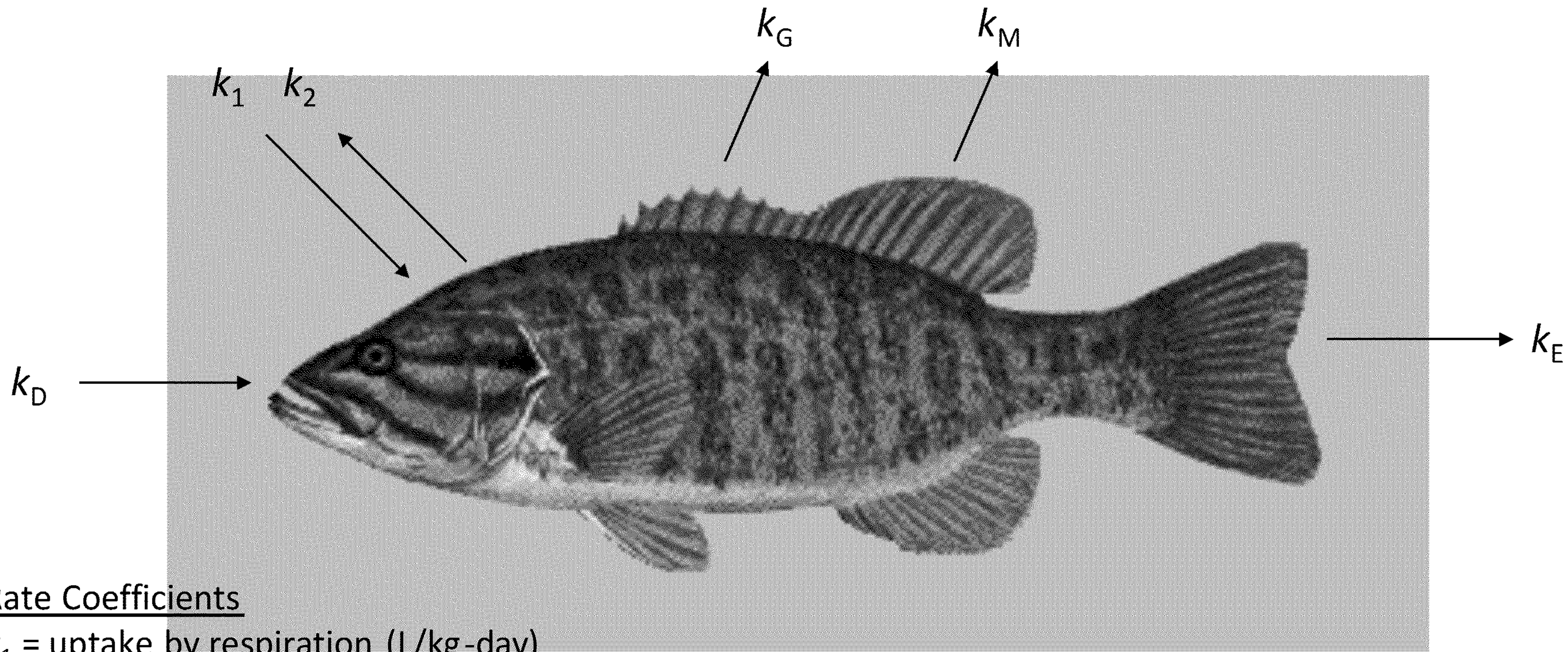
- Depth average is calculated as a layer thickness-weighted average in the water column and sediment bed
  - If using >10-layer average in the bed, calculates fractions of particulate and dissolved chemical concentration in the archive bed before depth averaging.
    - Assume fractions of particulate and dissolved chemicals in the archive bed is the same as those in the bottom layer (layer 10) of the active bed
    - $C_{tot,10} = C_{diss,10} + C_{part,10}$
    - $F_{diss,10} = C_{diss,10}/C_{tot,10}$
    - $F_{part,10} = 1 - F_{d,10}$
    - $C_{diss,archive} = C_{tot,archive} \times F_{d,10}$
    - $C_{part,archive} = C_{tot,archive} \times F_{p,10}$

# Exposure Zones (Segments)

# Model Segmentation

- Three primary segments
  - Estuarine (RM 0-4)
  - Transitional (RM 4-8.5)
  - Freshwater (RM 8.5-17.4)
- Define secondary segments based on other practical considerations
  - COPC concentrations
  - Human use
  - Feasibility
  - Currently set up to sub-divide the estuarine reach at RM 2 and the freshwater reach at RMs 12 and 15
- Calibration efforts to date focus on RM 0-8.5 (segment 11) and 8.5-Dundee Dam (segment 4)
- Set up to be able to model mudflats separately from the channel (mudflats provide important foraging habitat)

# Conceptual Model



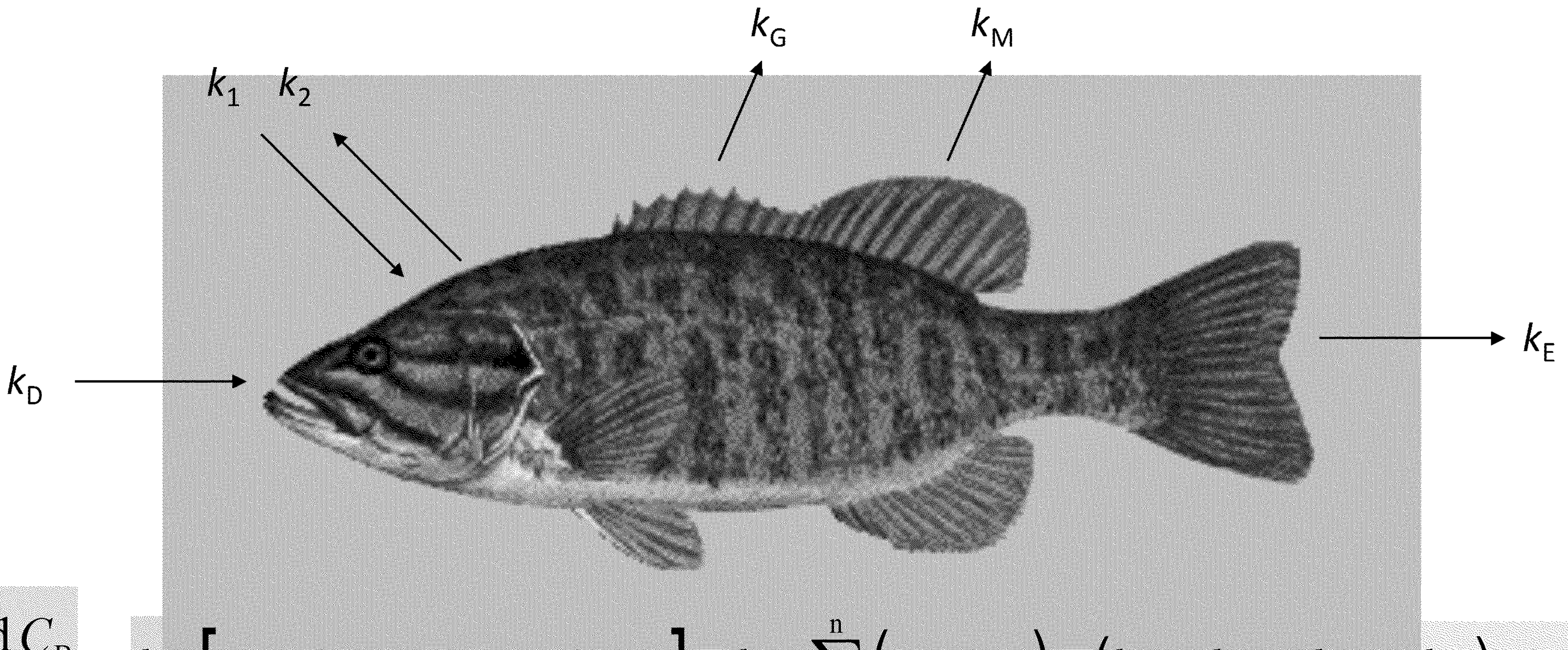

<u>Rate Coefficients</u>

$k_1$ = uptake by respiration (L/kg-day)
$k_2$ = elimination by respiration (/day)
$k_D$ = uptake by food and water ingestion (kg/kg-day)
$k_E$ = elimination by excretion/egestion (/day)
$k_M$ = elimination by metabolism (/day)
$k_G$ = dilution by growth (/day)

# Key Assumptions

- Whole-body tissue concentration model
  - Reasonable for chronic exposure to poorly metabolized hydrophobic organic chemicals (HOCs)
  - Appropriate when primarily concerned with risks to piscivorous wildlife or people
  - Use empirical fillet:whole body ratios to estimate fillet concentrations
- Important to be able to model dynamic exposure conditions
  - Valid for a remedial alternatives analysis tool
- Modeling average fish tissue concentrations
  - Appropriate because remedial action decisions expected to be driven by chronic human health risk reduction

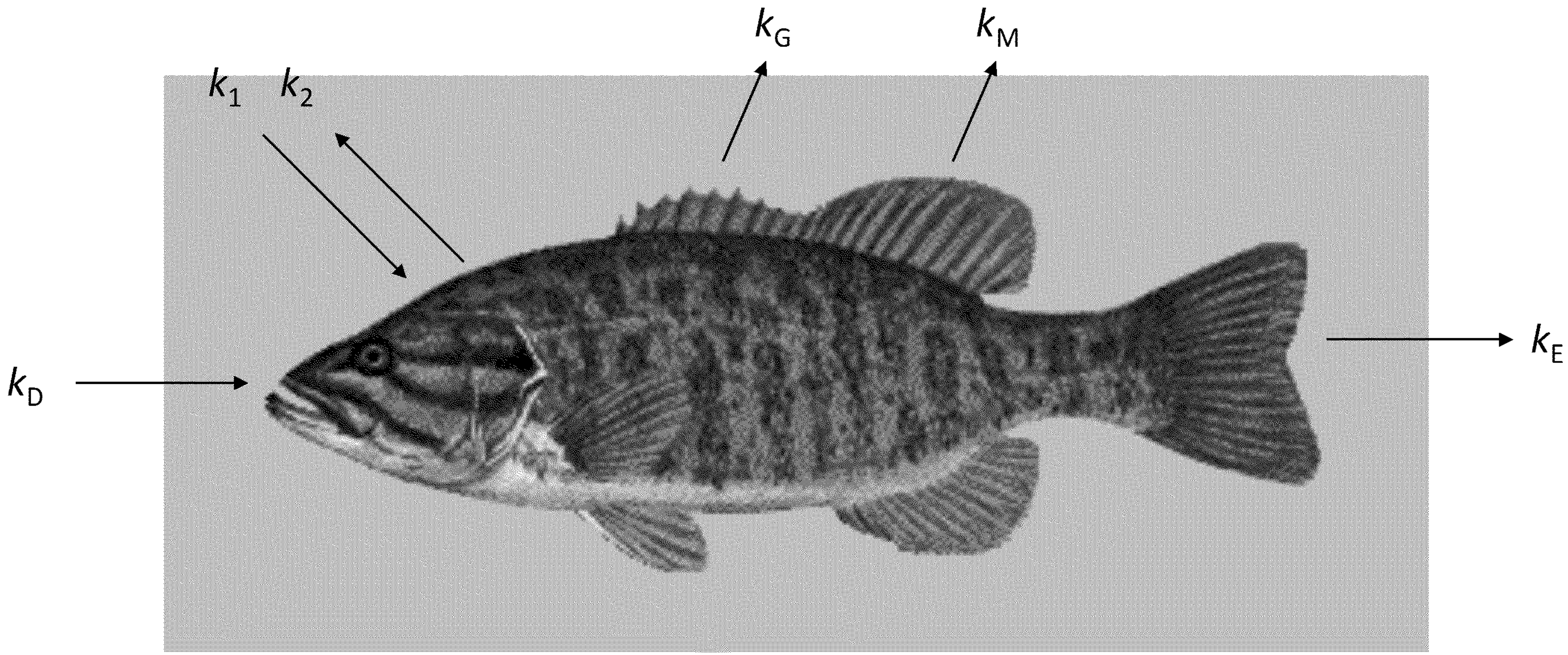
# Mathematical Model




$$\frac{\mathrm{d}\,C_B}{\mathrm{d}\,t} = \underbrace{k_1 \cdot \left[m_O \cdot C_{WD,O} + m_P \cdot C_{WD,S}\right]}_{\text{Respiratory uptake term}} + \underbrace{k_D \cdot \sum_{i=1}^{n}\left(P_i \cdot C_{D,i}\right)}_{\text{Ingestion uptake term}} - \underbrace{\left(k_2 + k_E + k_M + k_G\right) \cdot C_B}_{\text{Loss term}}$$

Rate of change of chemical concentration in the organism

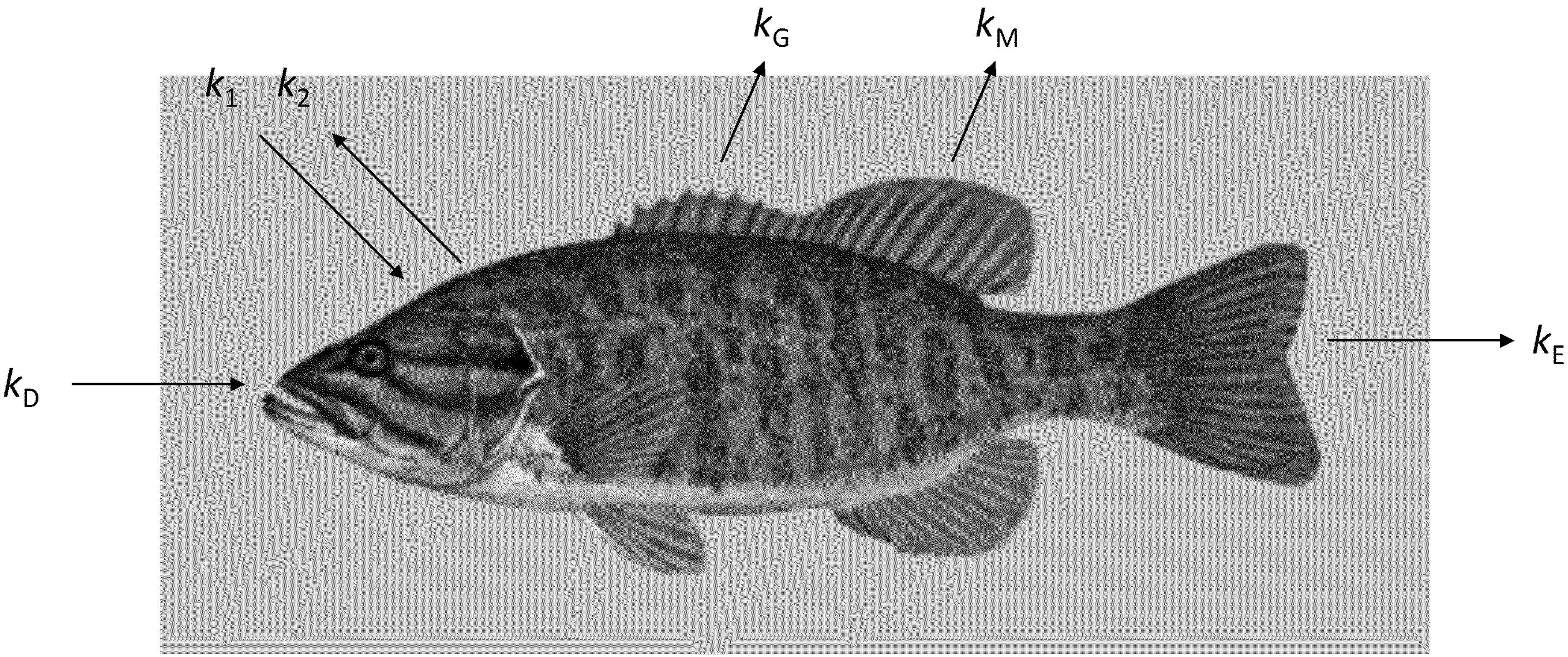
# Mathematical Model




$$\frac{\mathrm{d}\,C_B}{\mathrm{d}\,t} = k_1 \cdot \left[ m_O \cdot \boxed{C_{WD,O}} + m_P \cdot \boxed{C_{WD,S}} \right] + k_D \cdot \sum_{i=1}^{n} \left( P_i \cdot C_{D,i} \right) - \left( k_2 + k_E + k_M + k_G \right) \cdot C_B$$

Average dissolved chemical concentrations in overlying water and sediment pore water (from CFT)

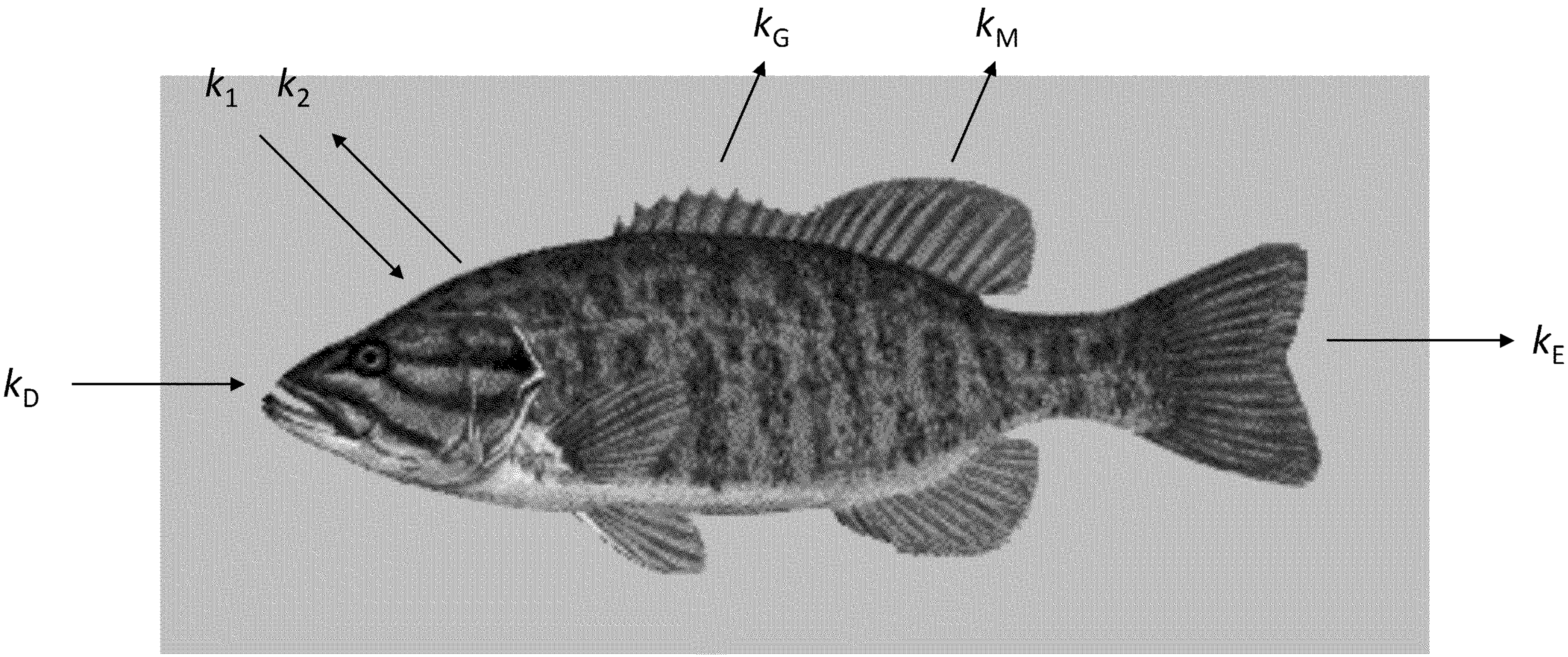
# Mathematical Model




$$\frac{dC_B}{dt} = k_1 \cdot \left[m_O \cdot C_{WD,O} + m_P \cdot C_{WD,S}\right] + k_D \cdot \sum_{i=1}^{n} \left(P_i \cdot C_{D,i}\right) - \left(k_2 + k_E + k_M + k_G\right) \cdot C_B$$

Ventilation fractions ($m_P = 1 - m_o$)

# Mathematical Model

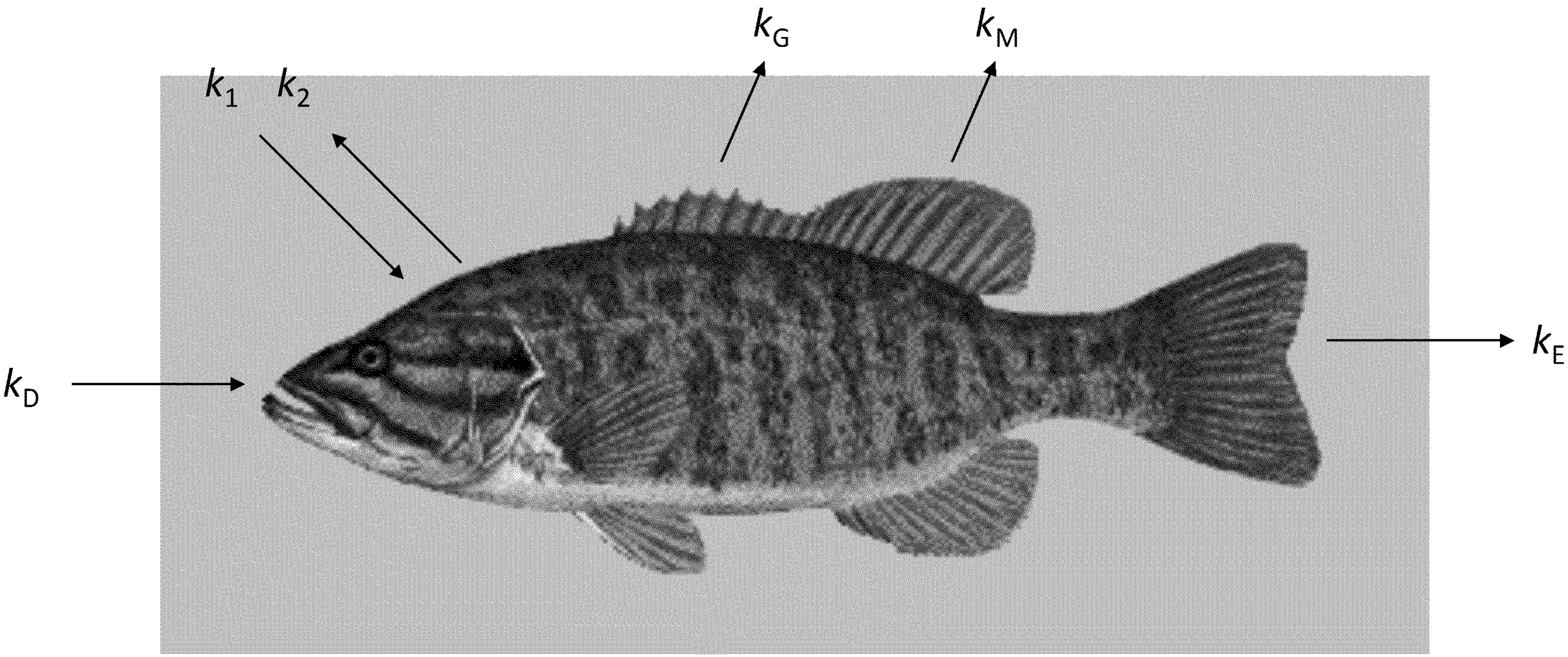



$$\frac{\mathrm{d}\,C_B}{\mathrm{d}\,t} = k_1 \cdot \left[ m_O \cdot C_{WD,O} + m_P \cdot C_{WD,S} \right] + k_D \cdot \sum_{i=1}^{n} \left( P_i \cdot C_{D,i} \right) - \left( k_2 + k_E + k_M + k_G \right) \cdot C_B$$

Prey fractions

Chemical conc. in prey type *i*

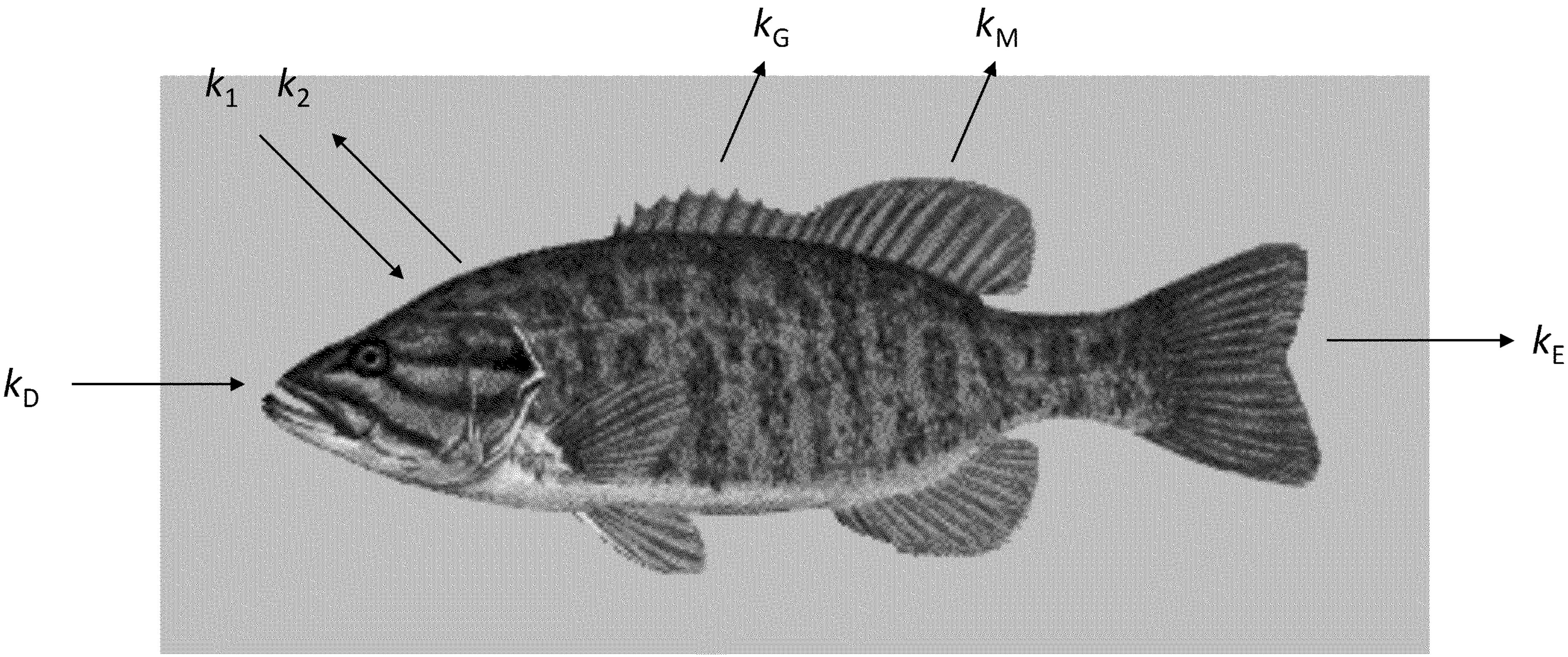
# Mathematical Model




$$\frac{\mathrm{d}C_B}{\mathrm{d}t} = k_1 \cdot \left[m_O \cdot C_{WD,O} + m_P \cdot C_{WD,S}\right] + k_D \cdot \sum_{i=1}^{n}\left(P_i \cdot C_{D,i}\right) - \left(k_2 + k_E + k_M + k_G\right) \cdot \boxed{C_B}$$

Chemical concentration
in the organism

# Mathematical Model




$$\frac{\mathrm{d}\,C_B}{\mathrm{d}\,t} = \boxed{k_1} \cdot \left[ m_O \cdot C_{WD,O} + m_P \cdot C_{WD,S} \right] + \boxed{k_D} \cdot \sum_{i=1}^{n} \left( P_i \cdot C_{D,i} \right) - \left( \boxed{k_2} + \boxed{k_E} + \boxed{k_M} + \boxed{k_G} \right) \cdot C_B$$

Uptake and loss rate coefficients

# $k_1$ for Fish, Benthic Invertebrates and Zooplankton

$$k_1 = \frac{E_W \cdot G_V}{W_B}$$

$E_W$ = gill chemical uptake efficiency

$$= \left(1.85 + \frac{155}{K_{ow}}\right)^{-1}$$

$K_{OW}$ = octanol − water partition coefficient

$G_V$ = ventilation rate (L/day)

$$= \frac{1{,}400 \cdot W_B^{0.65}}{C_{OX}}$$

$C_{OX}$ = dissolved oxygen (DO) concentration ($mg\ O_2/L$)

$$= (-0.24 \cdot T + 14.04) \cdot S$$

$T$ = temperature (°C)

$S$ = degree of oxygen saturation of the water column

So $k_1$ is a function of $K_{ow}$, body weight and DO concentration

# $k_1$ for Phytoplankton/Algae

$$k_1 = \frac{1}{A + B/K_{OW}}$$

where *A* and *B* are empirical constants describing aqueous and organic phase resistance to chemical uptake:

*A* = Normal($6\times10^{-5}$, $1\times10^{-5}$) (day) from Great Lakes field BCF data
*B* = Triang(1.8, 5.5, 9.2) (day) based on empirical data for various phytoplankton, algae, and cyanobacteria species as summarized by Arnot & Gobas (2004)

So phytoplankton $k_1$ is a function of $K_{ow}$

# $k_2$ for Fish, Benthic Invertebrates and Zooplankton

$$k_2 = \frac{k_1}{K_{BW}} = \frac{k_1}{\nu_{LB} \cdot K_{OW} + \nu_{NB} \cdot \beta \cdot K_{OW} + \nu_{WB}}$$

$$\begin{aligned}
\nu_{LB} &= \text{lipid fraction in the organism } \left(kg_{lipid} / kg_{organism,\ wet\ wt}\right) \\
\nu_{WB} &= \text{water fraction in the organism } \left(kg_{water} / kg_{organism,\ wet\ wt}\right) \\
\nu_{NB} &= \text{fraction non-lipid organic matter}^{*} \text{ (NLOM) } \left(kg_{NLOM} / kg_{organism,\ wet\ wt}\right) \\
&= 1 - \left(\nu_{LB} + \nu_{WB}\right) \\
\beta &= \text{sorption capacity of NLOM relative to lipid } \left(\beta = \text{Normal}\left(0.035, 0.005\right)\right)
\end{aligned}$$

So $k_2$ is a function of $K_{ow}$, body weight, DO concentration, and organism lipid and water fractions.

# $k_2$ for Phytoplankton/Algae

$$k_2 = \frac{k_1}{K_{BW}} = \frac{k_1}{\nu_{LB} \cdot K_{OW} + \nu_{NP} \cdot \gamma \cdot K_{OW} + \nu_{WB}}$$

$\nu_{LB}$ = lipid fraction in the organism $\left(kg_{lipid} / kg_{organism,\ wet\ wt}\right)$

$\nu_{WB}$ = water fraction in the organism $\left(kg_{water} / kg_{organism,\ wet\ wt}\right)$

$\nu_{NP}$ = fraction non - lipid organic carbon (NLOC) $\left(kg_{NLOC} / kg_{organism,\ wet\ wt}\right)$

$= 1 - \left(\nu_{LB} + \nu_{WB}\right)$

$\gamma$ = sorption capacity of NLOC relative to lipid $(\gamma = 0.350)$

So $k_2$ is a function of $K_{ow}$, body weight, DO concentration, and organism lipid and water fractions.

# Dietary Uptake Rate Coefficient

$$k_D = \frac{E_D \cdot G_D}{W_B}$$

$E_D$ = dietary chemical transfer efficiency

$$= \frac{1}{3.0 \times 10^{-7} \cdot K_{OW} + 2.0}$$

$G_D$ = feeding rate (kg/day)

$$= 0.022 \cdot W_B^{0.85} \cdot e^{0.06 \cdot T}$$

Exception : filter feeders

$G_D = G_V \cdot C_{SS} \cdot \sigma$

$C_{SS}$ = TSS concentration (kg/L)

$\sigma$ = particle scavenging efficiency (%)

So $k_D$ is a function of $K_{ow}$, body weight and water temperature.

- For filter feeders, $k_D$ is a function of body weight, DO concentration, TSS concentration and particle scavenging efficiency

$$k_E = \frac{E_D \cdot G_F \cdot K_{GB}}{W_B}$$

$$G_F = \text{fecal egestion rate } (\text{kg/kg - day})$$
$$= \{(1-\varepsilon_L)\cdot\nu_{LD} + (1-\varepsilon_N)\cdot\nu_{ND} + (1-\varepsilon_W)\cdot\nu_{WD}\}\cdot G_D$$

where :

$\varepsilon_L, \varepsilon_N$ and $\varepsilon_L$ are dietary adsorption efficiencies of lipid, NLOM and water

$\nu_{LD}, \nu_{ND}$ and $\nu_{WD}$ are overall fractions of lipid, NLOM and water in the diet

$$K_{GB} = \text{GI tract - organism partition coefficient}$$
$$= \frac{\nu_{LG}\cdot K_{OW} + \nu_{NG}\cdot\beta\cdot K_{OW} + \nu_{WG}}{\nu_{LB}\cdot K_{OW} + \nu_{NB}\cdot\beta\cdot K_{OW} + \nu_{WB}}$$

$\nu_{LG}, \nu_{NG}$ and $\nu_{WG}$ = lipid, NLOM and water contents in the gut $(\text{kg/kg}_{\text{wet wt}})$:

$$\nu_{LG} = \frac{(1-\varepsilon_L)\cdot\nu_{LD}}{(1-\varepsilon_L)\cdot\nu_{LD} + (1-\varepsilon_N)\cdot\nu_{ND} + (1-\varepsilon_W)\cdot\nu_{WD}}$$

$$\nu_{NG} = \frac{(1-\varepsilon_N)\cdot\nu_{ND}}{(1-\varepsilon_L)\cdot\nu_{LD} + (1-\varepsilon_N)\cdot\nu_{ND} + (1-\varepsilon_W)\cdot\nu_{WD}}$$

$$\nu_{WG} = \frac{(1-\varepsilon_W)\cdot\nu_{WD}}{(1-\varepsilon_L)\cdot\nu_{LD} + (1-\varepsilon_N)\cdot\nu_{ND} + (1-\varepsilon_W)\cdot\nu_{WD}}$$

$$k_E = \frac{E_D \cdot G_F \cdot K_{GB}}{W_B}$$

$$G_F = \text{fecal egestion rate (kg/kg - day)}$$
$$= \{(1-\varepsilon_L)\cdot \nu_{LD} + (1-\varepsilon_N)\cdot \nu_{ND} + (1-\varepsilon_P)\cdot \nu_{PD} + (1-\varepsilon_W)\cdot \nu_{WD}\}\cdot G_D$$

where :

$\varepsilon_L, \varepsilon_N, \varepsilon_P$ and $\varepsilon_L$ are dietary assimilation efficiencies of lipid, NLOM, NLOC and water

$\nu_{LD}, \nu_{ND}, \nu_{PD}$ and $\nu_{WD}$ are overall fractions of lipid, NLOM, NLOC and water in the diet

$$K_{GB} = \text{GI tract - organism partition coefficient}$$
$$= \frac{\nu_{LG}\cdot K_{OW} + \nu_{NG}\cdot \beta \cdot K_{OW} + \nu_{WG}}{\nu_{LB}\cdot K_{OW} + \nu_{NB}\cdot \beta \cdot K_{OW} + \nu_{WB}}$$

$$(\nu_{NG}\cdot \beta + \nu_{PG}\cdot \gamma)\cdot K_{OW}$$

$\nu_{LG}, \nu_{NG}, \nu_{PG}$ and $\nu_{WG}$ = lipid, NLOM, NLOC and water contents in the gut $(\text{kg/kg}_{\text{wet wt}})$:

$$\nu_{LG} = \frac{(1-\varepsilon_L)\cdot \nu_{LD}}{(1-\varepsilon_L)\cdot \nu_{LD} + (1-\varepsilon_N)\cdot \nu_{ND} + (1-\varepsilon_P)\cdot \nu_{PD} + (1-\varepsilon_W)\cdot \nu_{WD}}$$

$$\nu_{NG} = \frac{(1-\varepsilon_N)\cdot \nu_{ND}}{(1-\varepsilon_L)\cdot \nu_{LD} + (1-\varepsilon_N)\cdot \nu_{ND} + (1-\varepsilon_P)\cdot \nu_{PD} + (1-\varepsilon_W)\cdot \nu_{WD}}$$

$$\boxed{\nu_{PG} = \frac{(1-\varepsilon_P)\cdot \nu_{PD}}{(1-\varepsilon_L)\cdot \nu_{LD} + (1-\varepsilon_N)\cdot \nu_{ND} + (1-\varepsilon_P)\cdot \nu_{PD} + (1-\varepsilon_W)\cdot \nu_{WD}}}$$

$$\nu_{WG} = \frac{(1-\varepsilon_W)\cdot \nu_{WD}}{(1-\varepsilon_L)\cdot \nu_{LD} + (1-\varepsilon_N)\cdot \nu_{ND} + (1-\varepsilon_P)\cdot \nu_{PD} + (1-\varepsilon_W)\cdot \nu_{WD}}$$

Update to the Arnot & Gobas model that we are planning to implement, splitting out NLOM and NLOC fractions in the diet to account for 10-fold difference in partitioning of contaminant to NLOC and NLOM

# Egestion Loss Rate Coefficient

- So $k_E$ is a function of $K_{ow}$, body weight and water temperature, plus dietary adsorption efficiencies and overall fractions of lipid, NLOM, NLOC and water in the diet.
- For filter feeders, $k_E$ is a function of $K_{ow}$, body weight, TSS and DO concentrations, and particle scavenging efficiency.

$$k_G = a_G \cdot W_B^{-0.2}$$

$a_G$ = empirical constant

= 0.0005

So $k_G$ is a function of body weight.

Phytoplankton $k_G$ ~ Triang(0.03, 0.08, 0,13) (Arnot & Gobas 2004)

# Physical/Chemical Parameters

- $K_{ow}$[a, b]
- Chemical concentration in surface sediment
- Dissolved chemical concentration in the water column
- Dissolved organic carbon concentration
- Sediment total organic carbon concentration
- Dissolved chemical concentration pore water
- Total suspended solids concentration
- Particulate chemical concentration
- Water temperature
- Dissolved oxygen concentration[b]
- Tissue concentration data[b]

[a] All site-specific except $K_{ow}$
[b] All CFT output except $K_{ow}$, *TC* and *DO*

# Biological Parameters

- Many general biological parameters with ranges estimated from the scientific literature
- Site-specific weight, lipid fraction and water content data
- Metabolic rate constants
- Prey fractions

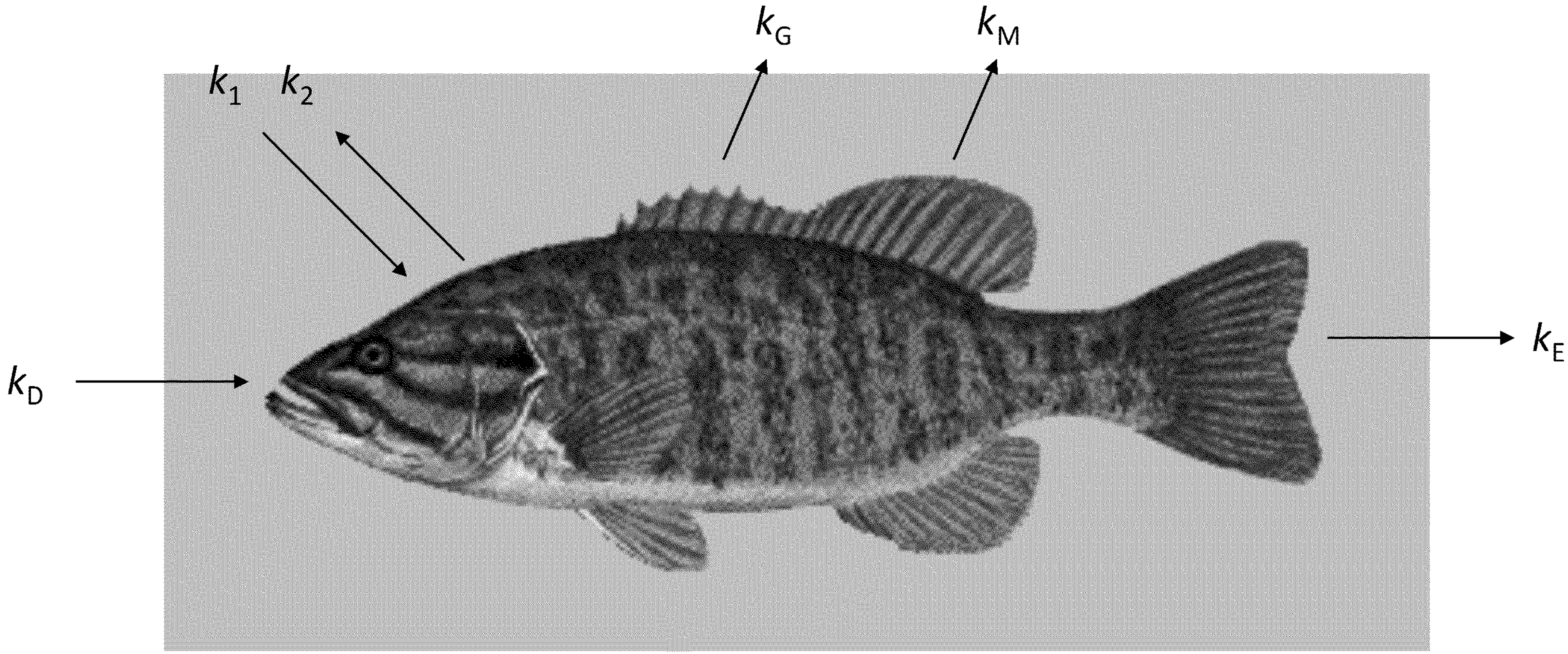
# Food Web

- Structured to be able to model up to 16 species
  - Phytoplankton/algae
  - Zooplankton
  - Benthic deposit feeders
  - Benthic detritivores
  - Small benthic omnivores
  - Large benthic omnivores
  - Filter feeding fish (e.g., menhaden)
  - Small forage fish (e.g., mummichog)
  - Blue crab
  - Smallmouth bass
  - Largemouth bass
  - White perch
  - White catfish
  - Channel catfish
  - Common carp
  - American eel

Some value in maintaining HHRA target species as separate species in the model

- Considering consolidating benthic trophic guilds, combining largemouth and smallmouth bass, and combining whit catfish and channel catfish.

# Food Web



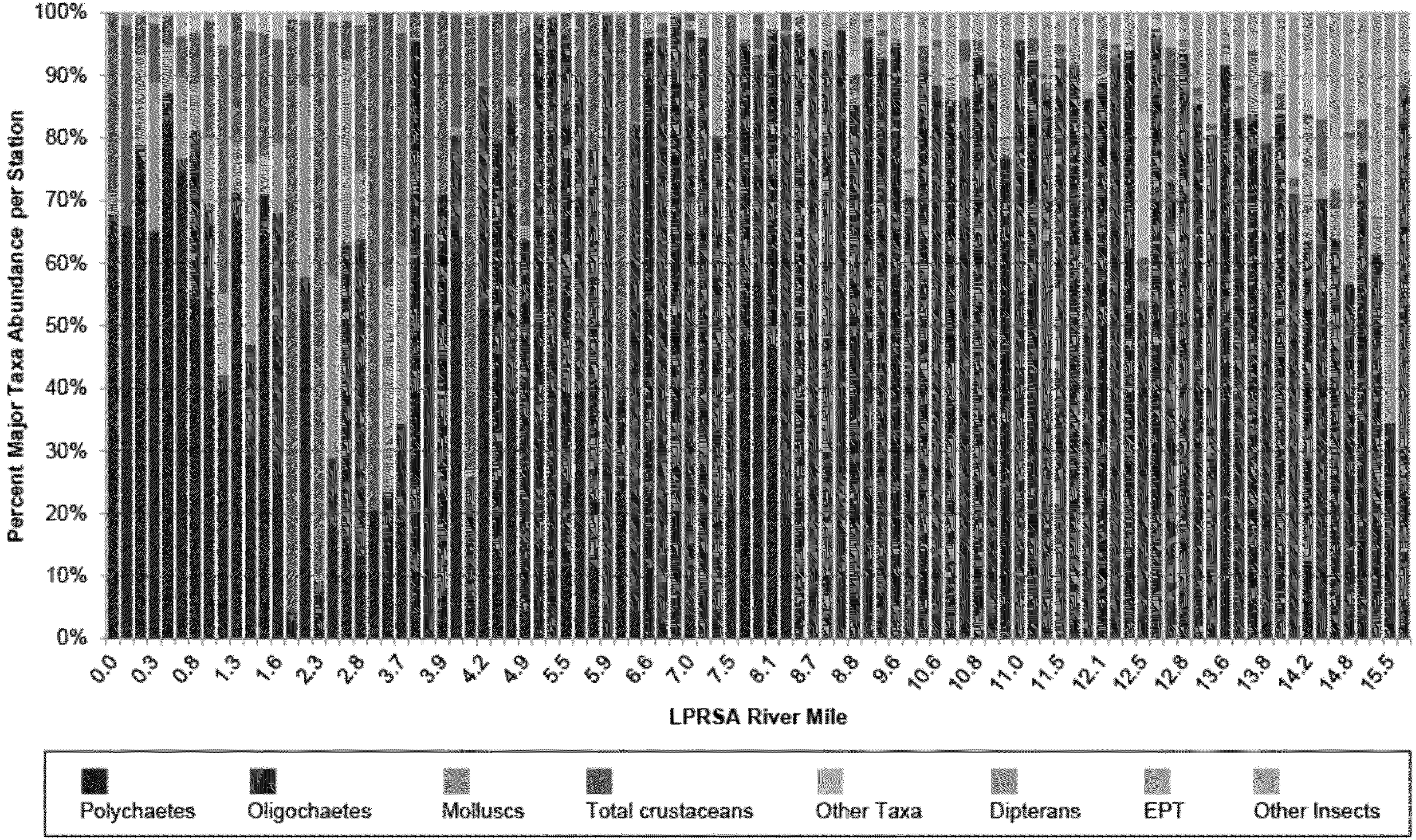

$$\frac{\mathrm{d}\,C_B}{\mathrm{d}\,t} = k_1 \cdot \left[m_O \cdot C_{WD,O} + m_P \cdot C_{WD,S}\right] + k_D \cdot \sum_{i=1}^{n} \left(P_i \cdot C_{D,i}\right) - \left(k_2 + k_E + k_M + k_G\right) \cdot C_B \qquad (1)$$

The model is a system of bioaccumulation equations of the form of equation (1), one for each component of the model's food web.

# BENTHIC COMMUNITY ANALYSIS/ BIOLOGICALLY ACTIVE ZONE

# LPRSA Salinity Zones for Benthic Community Analysis

# Benthic Community



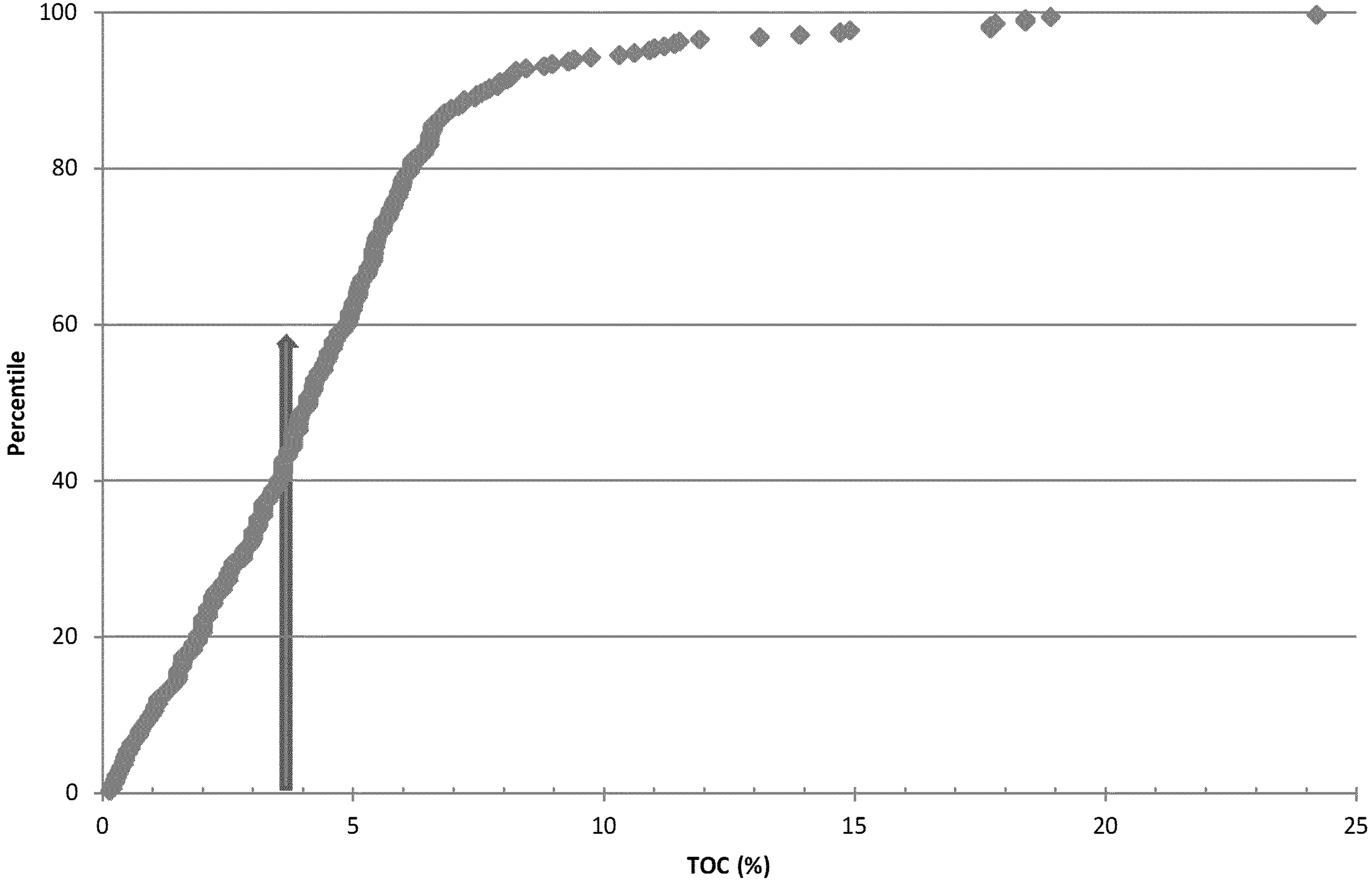
# Freshwater Community

# Estuarine Community

# Benthic Metrics by River Mile

# Benthic Diversity and Organic Enrichment

# % TOC
# 0 to 15 cm depth



# Depth of Biological Activity

# Data and Information Sources

- SPI Survey Data Report.
  - Germano and Associates, 2005
- Benthic Community sampling data
  - CPG, 2009
- Published literature

# Benthic Community Successional Stages

[redacted]

[redacted]

# LPRSA SPI Survey
# Germano and Associates, 2005

# Measured Parameters

- Eight parameters measured
  - Sediment type
  - Depositional layers
  - Surface boundary roughness
  - Sedimentary methane
  - Benthic habitat classifications
  - Apparent redox potential discontinuity (RPD) depth
  - Infaunal successional stage
  - Organism-sediment index
- Most relevant to question:
  - RPD depth
  - Evidence of activity below RPD depth
  - Members of benthic community and infaunal successional stage

# Summary

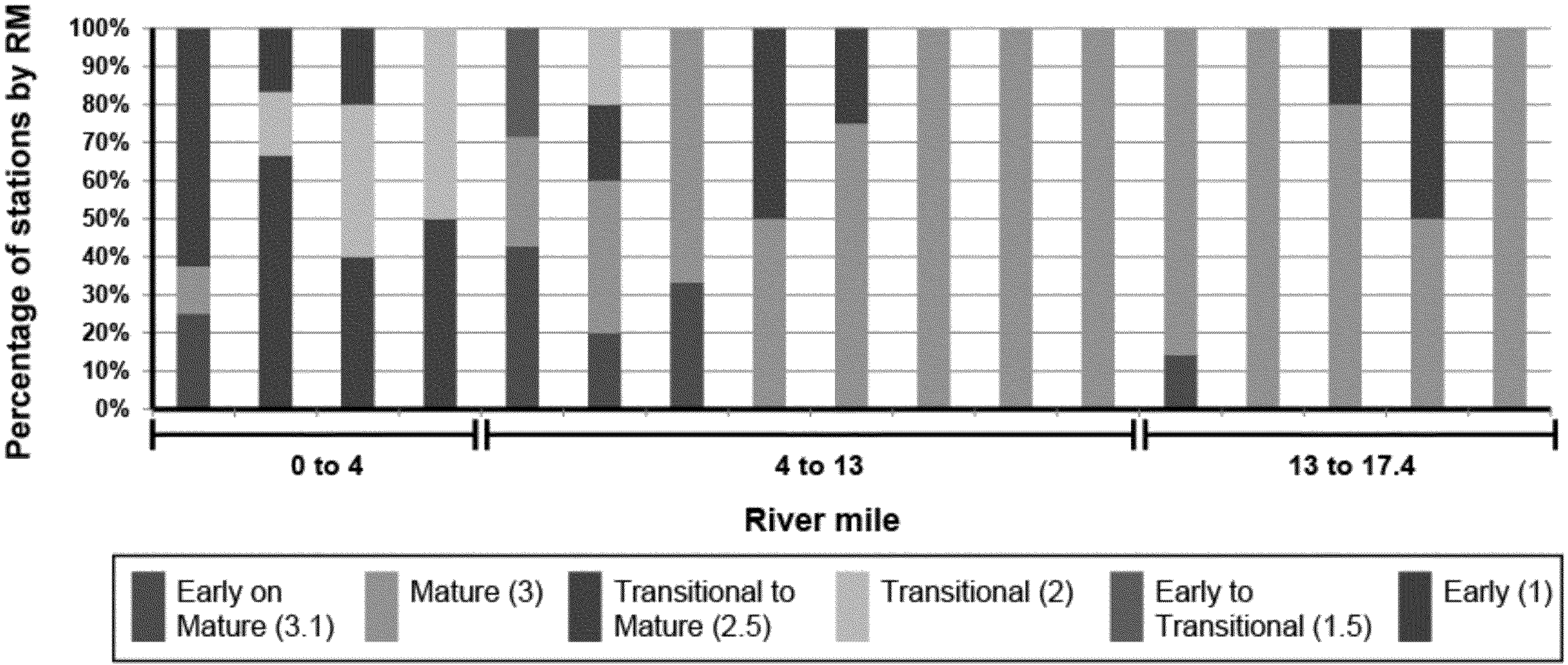
- Majority of the biological activity occurs above the RPD
- RPD in brackish water: 0.1 to 4.0 cm - mean of 1.6 cm
- RPD in freshwater: 0.4 to 5.0 cm with a mean of 1.9 cm
- In a few instances, feeding voids (relic or active) were observed below the RPD (3 – 12 cm)
- "Ubiquitous presence of subsurface layers of black, anoxic sediment having high apparent oxygen demand as well as methane being produced at depth"
- Successional stage
  - Brackish water: Mixture of successional stages but dominated by Stage I and Stage II
  - Freshwater: Supports a more advanced Stage III benthic community

# Benthic Community Data
# CPG data, 2009

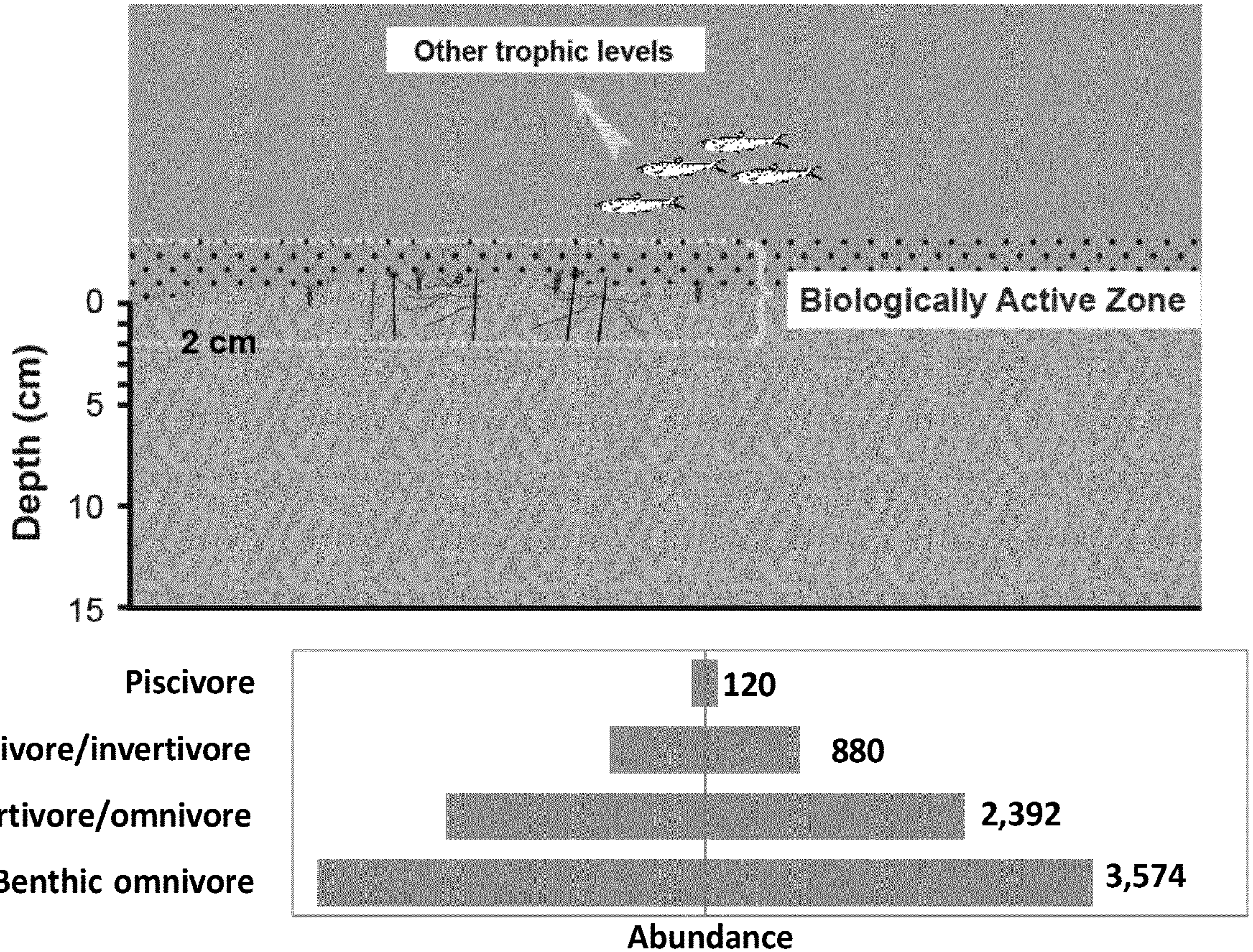
# Parameters used to stage species

- Opportunistic behavior
- Reproductive rate
- Longevity
- Body length, mass, and/or burrowing depth
- Association with stages as described in the literature

# Benthic Community Successional Stage



# Ecological Understanding



# Summary

- LPRSA has a mature benthic community that is consistent with expectations for a salt wedge estuary, predominately composed of detritivores and shallow deposit feeders
- Benthic organisms' chemical exposures occur predominately in the upper 2 cm of bedded sediment and overlying fluff layer

# CALIBRATION

# Calibration Approach

- Calibration done for two segments:
  - **RM 0 to 8.5** – corresponds to tissue collected from reaches 1 to 4
  - **RM 8.5 to Dundee Dam** – corresponds to tissue collected from reaches 5 to 8
- Calibration for entire width of river
  - i.e., not distinguishing mudflat areas at this time
    - Mudflats defined for the BERA as areas where the sediment surface is < -2ft MLLW, < 6° slope
    - Important foraging habitat

# Calibration Approach

- Based on steady state solution of the system of bioaccumulation equations

$$\frac{\mathrm{d}\,C_{\mathrm{B}}}{\mathrm{d}\,t} = 0 = k_1 \cdot \left[m_{\mathrm{O}} \cdot C_{\mathrm{WD,O}} + m_{\mathrm{P}} \cdot C_{\mathrm{WD,S}}\right] + k_{\mathrm{D}} \cdot \sum_{i=1}^{\mathrm{n}} \left(P_i \cdot C_{\mathrm{D},i}\right) - \left(k_2 + k_{\mathrm{E}} + k_{\mathrm{M}} + k_{\mathrm{G}}\right) \cdot C_{\mathrm{B}}$$

$$\left(k_2 + k_{\mathrm{E}} + k_{\mathrm{M}} + k_{\mathrm{G}}\right) \cdot C_{\mathrm{B}} = k_1 \cdot \left[m_{\mathrm{O}} \cdot C_{\mathrm{WD,O}} + m_{\mathrm{P}} \cdot C_{\mathrm{WD,S}}\right] + k_{\mathrm{D}} \cdot \sum_{i=1}^{\mathrm{n}} \left(P_i \cdot C_{\mathrm{D},i}\right)$$

$$C_{\mathrm{B}} = \frac{k_1 \cdot \left[m_{\mathrm{O}} \cdot C_{\mathrm{WD,O}} + m_{\mathrm{P}} \cdot C_{\mathrm{WD,S}}\right] + k_{\mathrm{D}} \cdot \sum_{i=1}^{\mathrm{n}} \left(P_i \cdot C_{\mathrm{D},i}\right)}{\left(k_2 + k_{\mathrm{E}} + k_{\mathrm{M}} + k_{\mathrm{G}}\right)}$$

# Calibration Approach

- Based on steady state solution of the system of bioaccumulation equations
- Calibrating primarily to tissue concentration data from the August-September 2009 fish tissue and decapod tissue collection effort
  - Tissue concentration data from the June-August 2010 small forage fish tissue collection effort provide a secondary LOE for checking model performance

# Calibration Dataset

| Species | Priority Level for Calibration | Count of Samples by Calibration Reach: RM 0 to 8.5 (Reaches 1 – 4) | Count of Samples by Calibration Reach: RM 8.5 to Dundee Dam (Reaches 5 – 8) |
|---|---|---|---|
| *Filter feeding fish* | *secondary* | *0 ** | *0 ** |
| *Small forage fish* | *secondary* | *18* | *12* |
| Blue crab | primary | 22 | 2 |
| Smallmouth bass | primary | 1 | 2 |
| Largemouth bass | primary | 0 | 3 |
| White perch | primary | 11 | 9 |
| White catfish | primary | 6 | 13 |
| Channel catfish | primary | 0 | 11 |
| Carp | primary | 4 | 8 |
| American eel | primary | 10 | 11 |

** Six menhaden samples from the 1999 Tierra dataset are available as a rough estimate for this species group*

# Calibration Approach

- Based on steady state solution of the system of bioaccumulation equations
- Calibrating primarily to tissue concentration data from the August-September 2009 fish tissue and decapod tissue collection effort
- Using SPAFs as quantitative model performance metrics

[redacted]

$$SPAF = \mathrm{Max}\left\{ \frac{\text{predicted } \overline{TC}}{\text{empirical } \overline{TC}}, \frac{\text{empirical } \overline{TC}}{\text{predicted } \overline{TC}} \right\}$$

$SPAF$ = species predictive accuracy factor

$\overline{TC}$ = mean tissue concentration

Consistency checks provide qualitative evaluation of performance

[redacted]

# Calibration Approach

- Based on steady state solution of the system of bioaccumulation equations
- Calibrating primarily to tissue concentration data from the August-September 2009 fish tissue and decapod tissue collection effort
- Using SPAFs as quantitative model performance metrics
- Calibration results to date are work in progress, for discussion purposes only, and subject to change
  - Preliminary work started with penta-CB (before we had CFT output)
    - Focused initially on RM 0-8.5
    - Individual PCB congeners (52, 118, and 187) used to test model performance
    - Preliminary calibration for PCB homologues as another model performance test
  - Currently focusing on 2,3,7,8-TCDD and tetra-CB
    - CFT output available; 2,3,7,8-TCDD is a step ahead of tetra-CB
  - Awaiting completion of HST and CFT to do final calibration
    - 2,3,7,8-TCDD and tri- through hepta-CBs
  - A lot of moving parts

# Initial Parameter Estimates

- Probability distribution functions (PDFs) or point estimates for bioaccumulation model parameters
  - Important that the PDFs encompass plausible ranges for the model parameters
  - Probabilities assigned to different values in the PDFs less important than the range of values
  - Preliminary sensitivity analyses helped identify parameters that were assigned point estimates
- Calibrated model is deterministic

# $K_{OW}$ Values

| Chemical | Log $K_{OW}$ Value<br>Nominal Value [a] | Distribution Minimum [b] | Distribution Maximum [b] |
|---|---|---|---|
| **PCB Homologues** | | | |
| Monochlorobiphenyl | 4.63 | 4.09 | 4.69 |
| Dichlorobiphenyl | 5.00 | 4.27 | 5.51 |
| Trichlorobiphenyl | 5.60 | 4.82 | 5.87 |
| Tetrachlorobiphenyl | 6.00 | 5.38 | 6.65 |
| Pentachlorobiphenyl | 6.45 | 5.94 | 7.20 |
| Hexachlorobiphenyl | 6.85 | 6.44 | 7.81 |
| Heptachlorobiphenyl | 7.22 | 6.80 | 8.27 |
| Octachlorobiphenyl | 7.63 | 7.14 | 9.08 |
| Nonachlorobiphenyl | 7.99 | 7.28 | 9.62 |
| Decachlorobiphenyl | 8.18 | 7.59 | 11.2 |
| **PCDDs/PCDFs** | | | |
| 2,3,7,8-TCDD | 6.38 | 5.38 | 8.93 |

[a] Nominal value is the mode of the triangular distribution. For PCB homologues, nominal values are from the CARP model (HydroQual 2007). CARP cited Hawker and Connell (1988) as the source for $K_{OW}$ values for PCB homologues in that model. The value for 2,3,7,8-TCDD was taken from the SPARC online database (2007).

[b] Maximum and minimum values are for individual congeners within a homologue group (Hawker and Connell 1988). 2,3,7,8-TCDD minimum and minimum values are from *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals* (Mackay et al. 2006).

# Chemical Concentrations in Surface Water

| Chemical | Detection Frequency | Concentration (ng/L) Distribution Value[a] Minimum | Maximum |
|---|---|---|---|
| **PCB Homologues** | | | |
| Monochlorobiphenyl | 29 of 32 | 0.033 | 0.049 |
| Dichlorobiphenyl | 32 of 32 | 0.56 | 0.85 |
| Trichlorobiphenyl | 32 of 32 | 2.52 | 4.41 |
| Tetrachlorobiphenyl | 32 of 32 | 4.00 | 7.97 |
| Pentachlorobiphenyl | 32 of 32 | 2.35 | 5.22 |
| Hexachlorobiphenyl | 32 of 32 | 1.53 | 4.13 |
| Heptachlorobiphenyl | 32 of 32 | 0.640 | 2.020 |
| Octachlorobiphenyl | 32 of 32 | 0.196 | 0.610 |
| Nonachlorobiphenyl | 32 of 32 | 0.062 | 0.165 |
| Decachlorobiphenyl | 32 of 32 | 0.036 | 0.098 |
| **PCDDs/PCDFs** | | | |
| 2,3,7,8-TCDD [b] | 30 of 31 | 0.0016 | 0.0051 |

Note: Surface water concentrations are based on validated August 2011 data and unvalidated February 2012 data collected by the CPG for locations in RM 0 through RM 8.

[a] The minimum and maximum define a uniform distribution. The minimum and maximum values are the minimum and maximum of the median values calculated for each sampling location (RM 0, RM 1.4, Tidal 1, and Tidal 2). Each median included the deep and shallow samples across all tidal conditions for both sampling events (i.e., eight samples were included in calculation of each median).

[b] An unusually high sample from RM 6.7 (Tidal 2) collected during an ebb tide was omitted from the dataset. The validated concentration for this sample was several orders of magnitude higher than that for any other chemical in the surface water samples.

# Crab PCB Metabolism Rate Coefficients

| PCB Homologue | $k_M$ Distribution Minimum [a] | $k_M$ Distribution Maximum [a] |
|---|---|---|
| Tetra-CB | 0 | 0.008 |
| Penta-CB | 0 | 0.008 |
| Hexa-CB | 0 | 0.008 |

Note: Metabolism rate coefficients are expressed as fraction per day.

[a] Species-specific studies indicate that several crab species (*Macropipus tuberculatus*, *Necora puber,* and *Cancer pagurus*) have a strong capacity (relative to mussels and fish) to metabolize certain PCB congeners (Porte and Albaiges 1993; Bodin et al. 2007).These three homologues include congeners found to be strongly metabolized in crab (Porte and Albaiges 1993). A uniform distribution was used for this parameter because of the high uncertainty in its value. In the absence of species-specific data, the range is generally based on the best-estimate metabolism rate coefficients for PCB congeners for fish reported in Arnot et al. (2008).

# 2,3,7,8-TCDD Metabolism Rate Coefficients

| Species Group | Selected $k_M$ | |
|---|---|---|
| | Distribution Minimum [a] | Distribution Maximum [a] |
| Invertebrates | 0.007 | 0.024 |
| Fish | 0.007 | 0.024 |
| Carp | 0.0016 | 0.056 |
| American eel | 0.0016 | 0.082 |

Note: Metabolism rate coefficients are expressed as fraction per day.

[a] Values are from Arnot *et al.* (2008); estimates were provided only for fish. A uniform distribution was used for this parameter because of the high uncertainty in its value. The minimum and maximum are the minimum and maximum best-estimate values reported. Species-specific values were available for carp, so the 2.5 and 97.5 percentile estimates reported for carp (Arnot *et al.* 2008) were used as the maximum and minimum for this species. The range for American eel reflect the range of 2.5 and 97.5 percentiles reported for any species (Arnot *et al.* 2008) because species-specific data were unavailable.

# Physical/Chemical Parameters

| Parameter | Unit | Nominal Value | Distribution Type | Distribution Value or Range of Values | Source Notes |
|---|---|---|---|---|---|
| OC content of sediment | percent | 4.32 | normal | SD = 0.22 | SWAC is based on 2008, 2009, and 2010 surface sediment data between RM 0 and RM 8; SE is calculated using arithmetic mean/SD of data. |
| Mean water temperature | °C | 14.9 | normal | SD = 2.6 | Based on monthly averages calculated using data from AECOM (Wayne 2011). |
| Concentration of suspended solids | kg/L | $2.5\times 10^{-5}$ | uniform | $1.6 \times 10^{-5}$ – $2.5 \times 10^{-5}$ | Water concentrations are based on validated August 2011 data and unvalidated February 2012 data collected by the CPG for locations in RM 0 through RM 8. The minimum and maximum define a uniform distribution. The minimum and maximum values are the minimum and maximum of the median values calculated for each sampling location (RM 0, RM 1.4, Tidal 1, and Tidal 2). Each median included deep and shallow samples across all tidal conditions for both sampling events (i.e., eight samples were included in the calculation of each median)(AECOM 2011). |

# General Biological Parameters

| Parameter | Unit | Nominal Value | Distribution Type | Source Notes |
|---|---|---|---|---|
| Uptake constant A | none | $6.0 \times 10^{-5}$ | point | Gobas and Arnot (2004; 2005) |
| Uptake constant B | none | 5.50 | point | Gobas and Arnot (2004; 2005) |
| Dietary transfer efficiency constant A | none | $3 \times 10^{-7}$ | point | Arnot and Gobas (2004) |
| Dietary transfer efficiency constant B | none | 2.0 | point | Arnot and Gobas (2004) |
| NLOM-octanol proportionality constant | none | 0.035 | point | Arnot and Gobas (2004) |
| NLOC-octanol proportionality constant | none | 0.35 | point | Arnot and Gobas (2004) |

# Species-Specific Parameters

- Based on available site-specific data or on data available from the literature
- Working draft, subject to change
- Link to species-specific parameter tables

# Preliminary Calibration

- Ran Monte Carlo simulations on the uncalibrated steady state model for the two calibration reaches (penta-CB)
- Outputs compared with average TCs (by species) in the calibration dataset for the two calibration reaches
- Monte Carlo runs that produced relatively low SPAFs retained for further testing
- Model runs were winnowed down by evaluating their performance across multiple chemicals and fish species
  - The parameter set used in the calibrated model performed well across chemicals and species
  - Consistency across reaches
  - Consistency across correlated parameters, with other LPRSA models

# Preliminary Calibration for Non-Chemical-Specific Parameters

- Non-chemical-specific parameters were calibrated for pentaCB
  - Calibration distributions for TSS, POC and DOC developed using empirical data from the CPG August 2011 event
    - Final bioaccumulation model calibration will use calibrated CFT output for these site-specific parameters
  - Rough, preliminary SWAC estimates calculated by Windward using natural neighbors interpolation of surface sediment concentrations
  - Uncalibrated nominal values for chemical-specific calibration parameters (pentaCB water concentration and $K_{ow}$)
- Best-performing pentaCB model run provided calibrated parameter values for non-chemical-specific parameters

# Sensitivity Analysis

- Identified sensitive parameters by calculating Pearson product-moment correlation coefficients between input parameters and predicted tissue concentrations
  - Parameters that affected predictions for multiple species were those related to general uptake and exposure (e.g., $K_{ow}$ and chemical concentration in water) and factors used to calculate particulate and detritus concentrations (e.g., concentration of suspended solids, particulate organic carbon).
    - Particulates and detritus are the primary foods for small benthic detritivores, which are the most prevalent benthic species.
  - Model predictions for individual species were also sensitive to their own species-specific parameters, such as lipid content and diet
- Sensitive parameters' values were consistent across best performing model runs

# Testing

- Calibrated non-chemical-specific parameter set used to predict tissue concentrations for PCBs 52, 118, and 187
  - Congeners selected to cover broad $K_{ow}$ range
  - Uncalibrated nominal values used for chemical-specific parameters (water concentrations and $K_{ow}$s)
- All three congener models generally performed well when parameterized with the pentaCB-calibrated non-chemical-specific parameter set

# Preliminary Calibration for Chemical-Specific Parameters

- $K_{ow}$s and water concentrations calibrated for each of the PCB homologs and 2,3,7,8-TCDD using the Monte Carlo simulation technique summarized above
  - Calibrated values for non-chemical-specific parameters
  - Chemical metabolism rate coefficients ($k_m$s) set to 0
  - Model outputs sorted from highest to lowest average SPAF across target species
  - Model performance examined for non-target species
  - $K_{ow}$s checked for consistency with expectations
    - Increasing with degree of chlorination
    - Similar to values selected for the New York/New Jersey Estuary Program's Contamination Assessment and Reduction Project model

# Testing Preliminary Chemical-Specific Parameter Calibration

- Predicted concentrations from calibrated PCB homolog models summed and compared to empirical total PCB congener concentrations
  - *Important performance check because the end use of the homolog models is to predict total PCB concentrations by summing the homologs*

# $k_M$ Calibration

- $k_M$ calibrated for 2,3,7,8-TCDD using the Monte Carlo simulation technique summarized above
  - American eel and carp calibrated separately from other fish species
    - Literature indicates that eel are more rapid and carp are slower metabolizers of dioxins than other fish species
    - Dioxin elimination times for carp >10x longer than for guppy, fathead minnow (Opperhuizen and Sijm 1990)
    - Empirical concentrations for TCDD in carp much higher than for higher trophic status species from same location (*ibid.*)
    - Study of bioaccumulation patterns for various organic compounds in European eel found extremely low bioaccumulation of dioxin and furan congeners was extremely low most likely due to reduced uptake, effective metabolic clearance, or both (Van der Oost, Opperhuizen et al. 1996).
  - Invertebrates calibrated separately from fish
  - Model outputs sorted from highest to lowest average SPAFs across target species, model performance examined for non-target species, results used to select calibrated $k_M$s

# $k_M$ Citations

Opperhuizen, A. and D. T. H. M. Sijm. 1990. Bioaccumulation and biotransformation of polychlorinated dibenzo-p-dioxins and dibenzofurans in fish. *Environ Toxicol Chem* **9**: 175-186.

Van der Oost, R., A. Opperhuizen, *et al.* 1996. Biomonitoring aquatic pollution with feral eel (*Anguilla anguilla*). I. Bioaccumulation: biota-sediment ratios of PCBs, OCPs, PCDDs and PCDFs. *Aqua Tox* **35**: 21-46.

# Preliminary Calibration Results

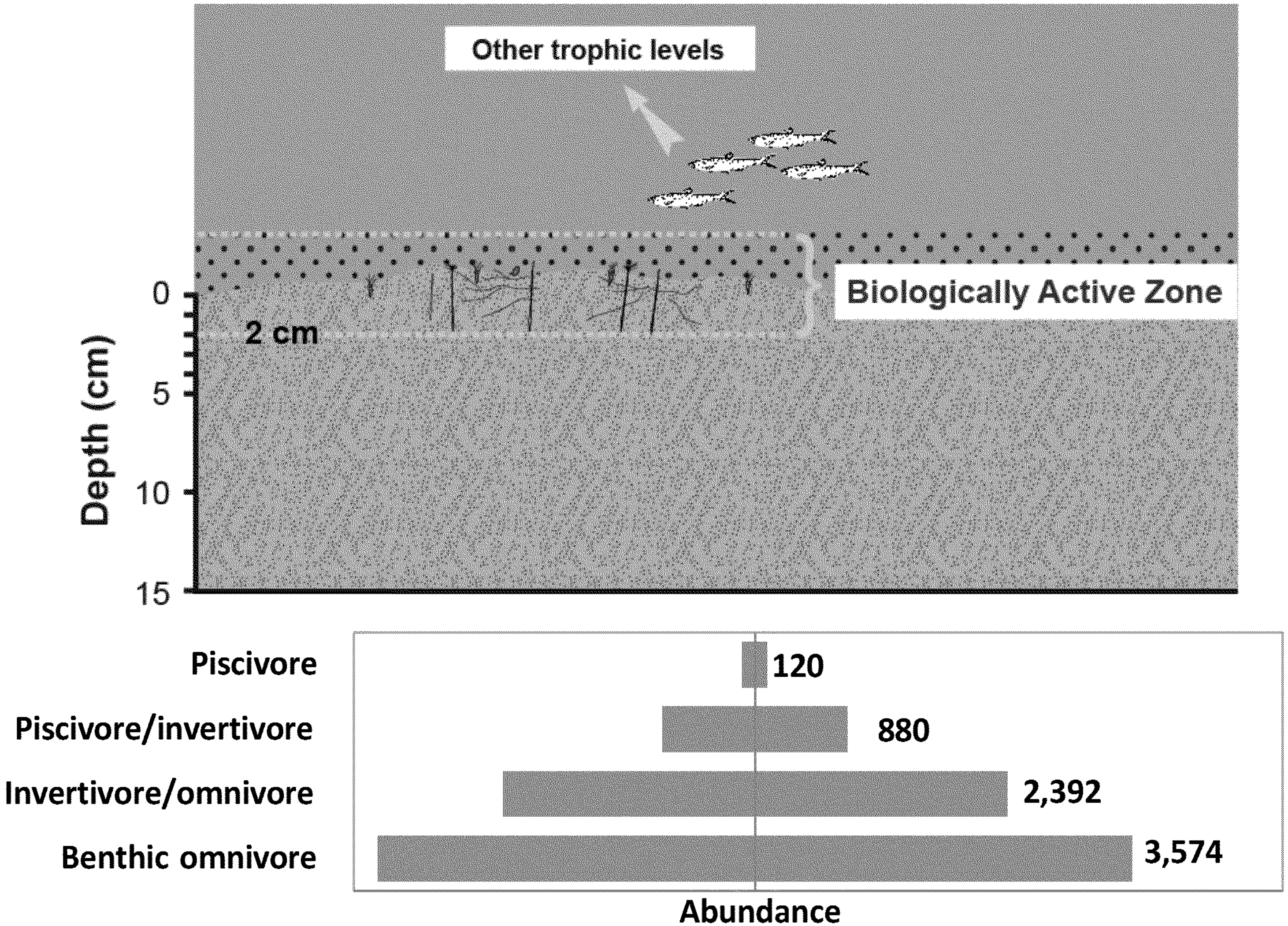
## April 2012 SPAFs, RM 0-8.5

| Chemical | Small Forage Fish | Blue Crab | Smallmouth Bass | White Perch | White Catfish | Carp | American Eel |
|---|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | **2.9** | **2.6** | **3.4** | 1.0 | **1.1** | 1.2 | **1.2** |
| Total PCBs | **1.8** | **3.6** | **3.6** | **1.6** | 1.0 | 1.3 | **1.3** |

**Bold=overprediction**

- Tissue concentrations surprisingly low given sediment concentrations
- Physical/chemical parameters consistent with literature
- Suggests compressed food chain
- Apparent exposure concentrations for benthic fauna more consistent with near-bottom particulates than bedded sediment

# Ecological Understanding



# Preliminary Calibration Refinements

- Site-specific parameters provided by the CFT
- Focusing on 2,3,7,8-TCDD and tetra-CB
- Both calibration reaches
- No full recalibration until the HST and CFT are ready; instead we are:
  - updating the site-specific inputs based on CFT outputs
  - checking effects on model performance
  - making minor adjustments
  - a lot of moving parts

# Interim Draft Results

November 2013 SPAFs, RM 0-8.5

| Chemical | Small Forage Fish | Blue Crab | Smallmouth Bass | White Perch | White Catfish | Carp | American Eel |
|---|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | **4.5** | 1.0 | **3.1** | 1.1 | 1.7 | **1.4** | **1.5** |
| Tetra-CB | 1.0 | 1.4 | **2.7** | 1.6 | **1.2** | **1.4** | 1.2 |

April 2012 SPAFs, RM 0-8.5

| Chemical | Small Forage Fish | Blue Crab | Smallmouth Bass | White Perch | White Catfish | Carp | American Eel |
|---|---|---|---|---|---|---|---|
| 2,3,7,8-TCDD | **2.9** | **2.6** | **3.4** | 1.0 | **1.1** | 1.2 | **1.2** |
| Total PCBs | **1.8** | **3.6** | **3.6** | **1.6** | 1.0 | 1.3 | **1.3** |

Steady state bioaccumulation model template

# Model Comparison to BSAFs Used in the Draft FFS

| Source | Small Forage Fish | Blue Crab | Piscivorous Fish [a] |
|---|---|---|---|
| Draft Focused Feasibility Study (TEQ D/F) | 0.10 | 0.15 | 0.20 |
| Preliminary Working Draft Bioaccumulation Model (2,3,7,8-TCDD) | 0.21 | 0.06 | 0.13 |

[a] Mean of smallmouth bass, largemouth bass, and white perch

# USING THE MODEL TO MAKE TISSUE CONCENTRATION PROJECTIONS FOR REMEDIAL ALTERNATIVES ANALYSIS

# Tissue Concentration Projections

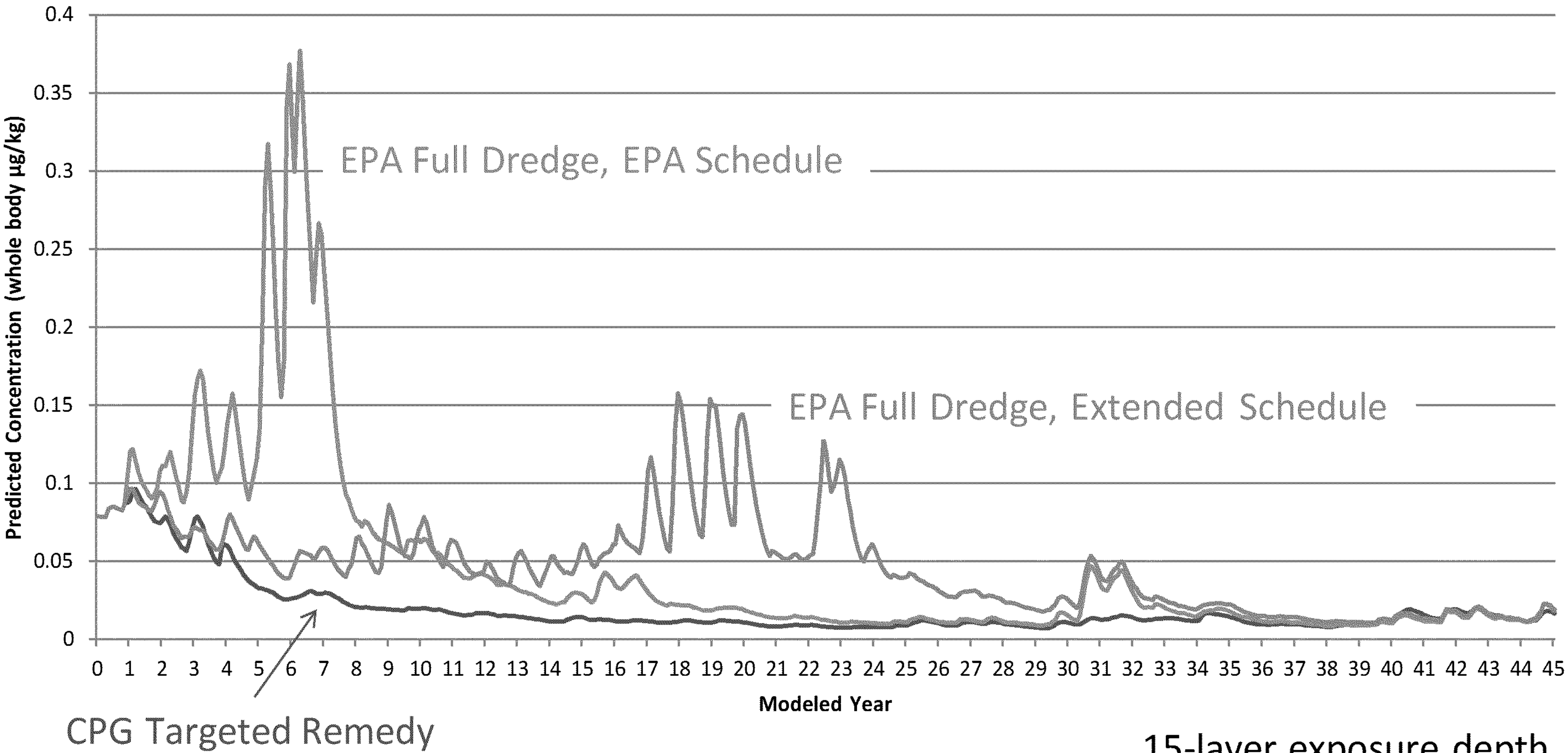
- Dynamic version of the model used to project changes in tissue concentrations over time for potential remedial alternatives
- Dynamic model is a system of difference equations:

$$C_{\mathrm{B}}(t+\Delta t)=\frac{C_{\mathrm{B}}(t)+\Delta t\cdot\left(k_1\cdot\left[m_{\mathrm{O}}\cdot C_{\mathrm{WD,O}}(t+\Delta t)+m_{\mathrm{P}}\cdot C_{\mathrm{WD,S}}(t+\Delta t)\right]+k_{\mathrm{D}}\cdot\sum_{i=1}^{n}\left[P_i\cdot C_{\mathrm{D},i}(t+\Delta t)\right]\right)}{1+\Delta t\cdot\left\{\left(k_2+k_{\mathrm{E}}+k_{\mathrm{M}}+k_{\mathrm{G}}\right)\right\}}$$

- Static parameters set to interim calibrated values
- Time-varying site-specific inputs from CFT
- Bioaccumulation model provides apples-to-apples comparison
  - Same model applied to all alternatives
  - Differences in TC projections reflect differences in projected exposures
  - Future TCs uncertain but relative comparisons are informative

# White Perch RM 0-8.5

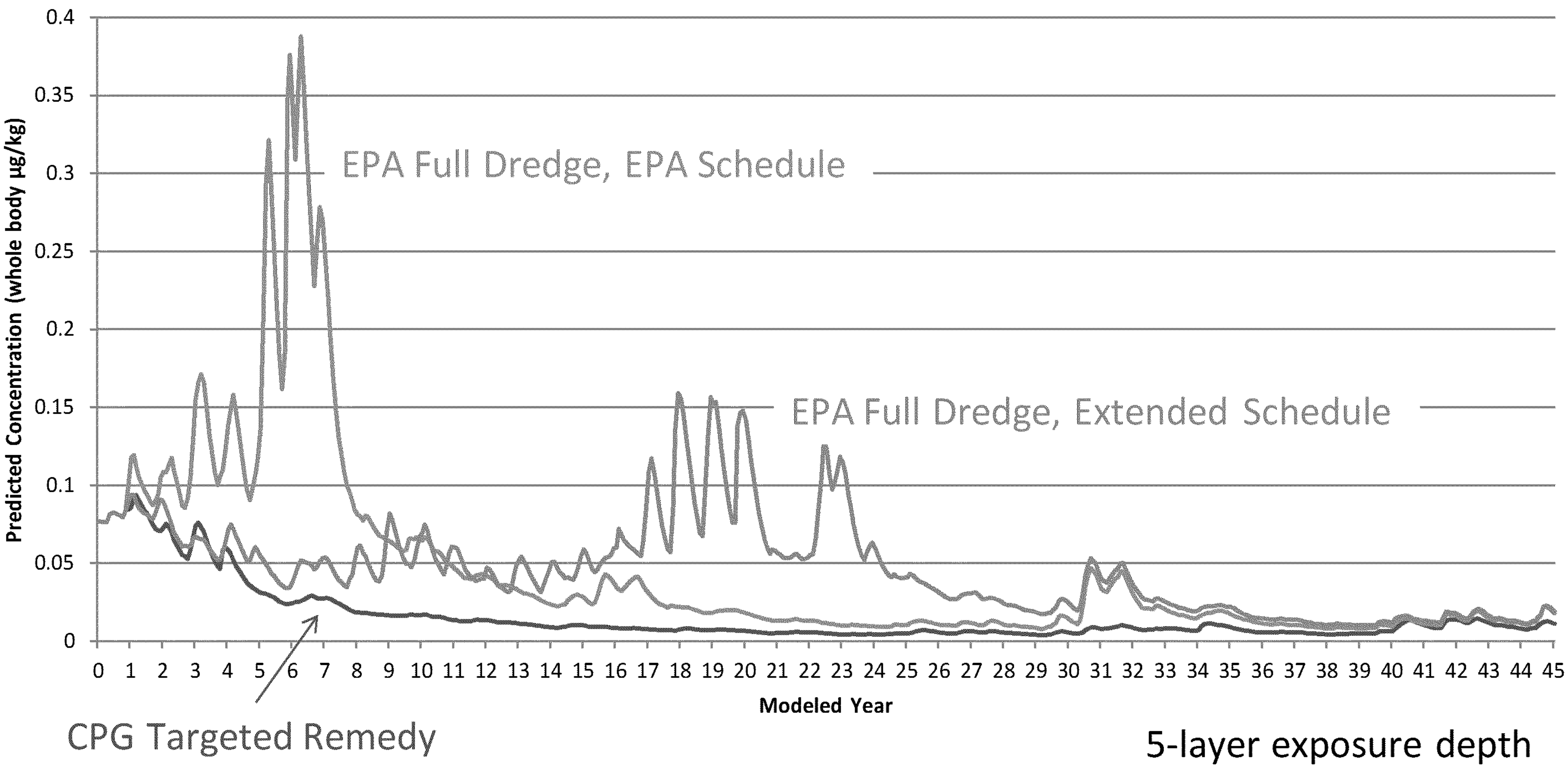
## 2,3,7,8-TCDD




15-layer exposure depth

# White Perch RM 0-8.5

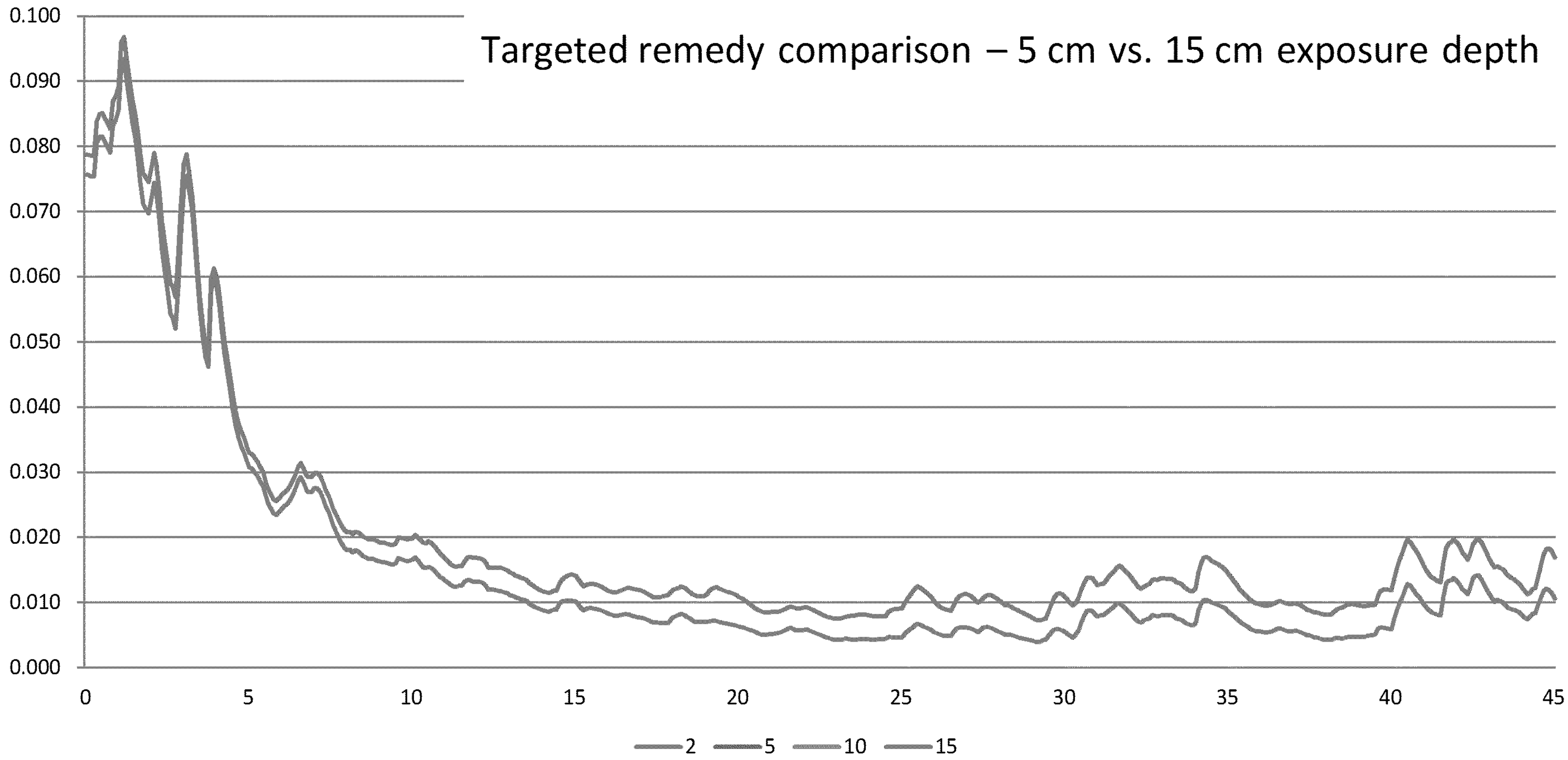
## 2,3,7,8-TCDD




5-layer exposure depth

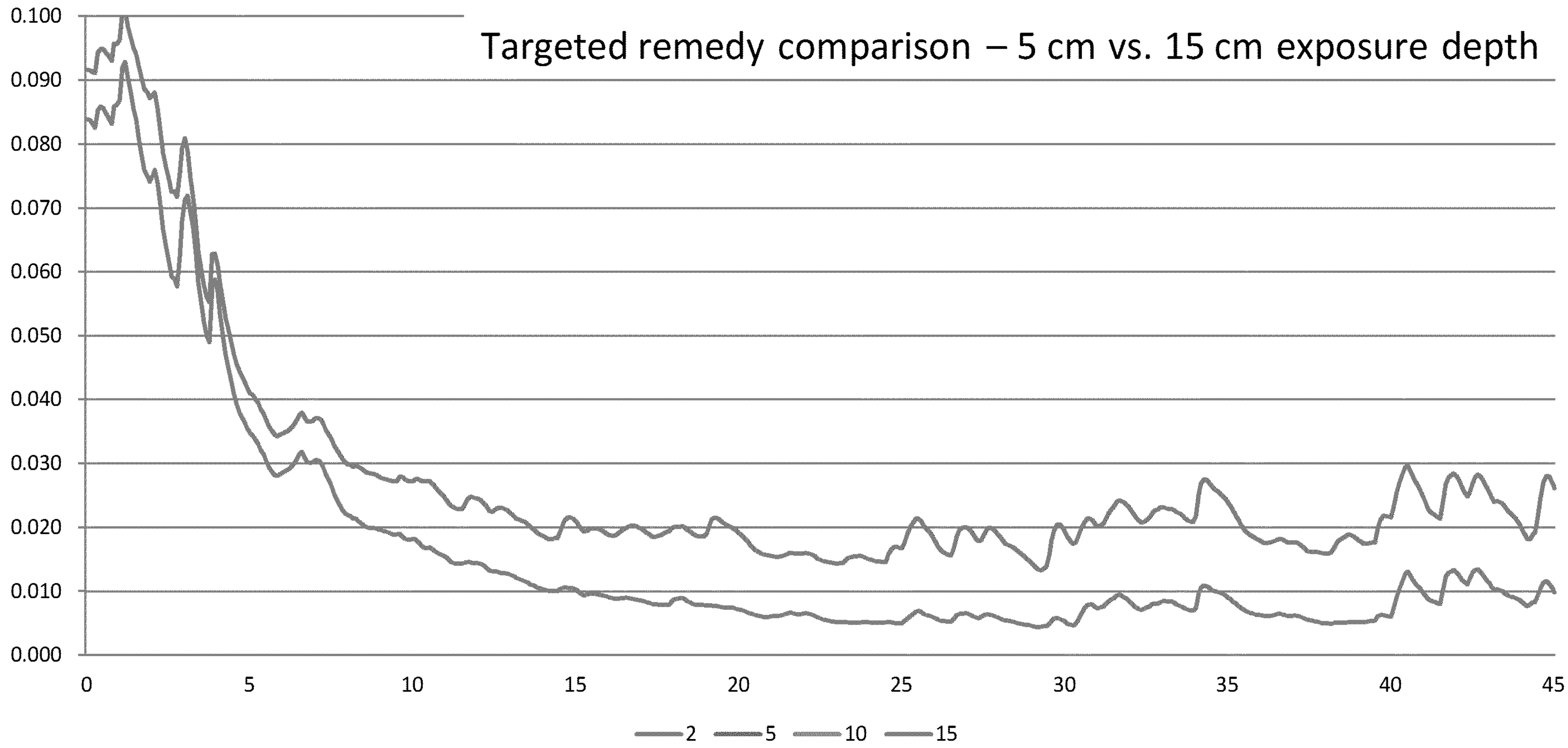
# White Perch RM 0-8.5

## 2,3,7,8-TCDD

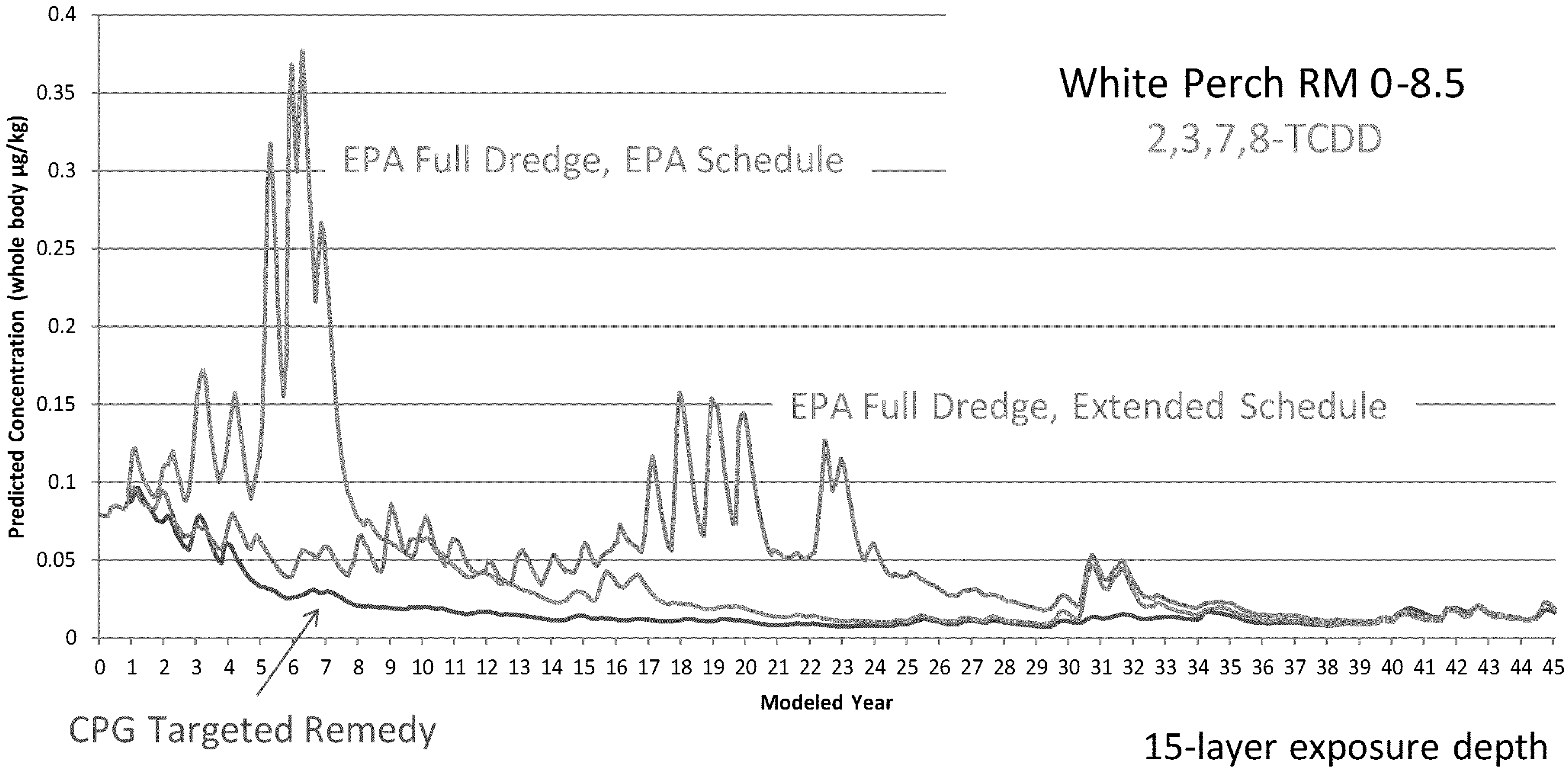


# White Catfish RM 0-8.5

## 2,3,7,8-TCDD



- The exposure depth assumption makes a difference of about a factor of 2 in post-remediation tissue concentration projections for the targeted remedy. The more important take-away is that the models are telling us that the targeted remedy would be more effective at reducing environmental exposures to 2,3,7,8-TCDD than a more invasive remedy would be.



# Agenda

- Bioaccumulation model
  - Background information
  - Model structure
- Benthic community analysis/biologically active zone
- Calibration
  - Data
  - Approach
  - Preliminary results
- Using the model to make projections for remedial alternatives analysis
  - Dynamic model
  - Preliminary projections
- Open discussion
- Wrap up/next steps
  - Additional oversight